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## Cyanide Chemistry—Precious Metals Processing and Waste Treatment

By Charles M. Flynn, Jr., and Sandra McGill Haslem

**UNITED STATES DEPARTMENT OF THE INTERIOR**  
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## UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

### Metric

cm	centimeter	mg • L <sup>-1</sup>	milligram per liter
cm <sup>-1</sup>	reciprocal centimeter	min	minute
cm <sup>-1</sup> • M <sup>-1</sup>	reciprocal centimeter per mole per liter	mm	millimeter
g • L <sup>-1</sup>	gram per liter	mol	mole
h	hour	mol <sup>-1</sup>	reciprocal mole
J	joule	mol • L <sup>-1</sup>	mole per liter
J	joule per kelvin	(mol • L <sup>-1</sup> ) <sup>-1</sup> • Pa <sup>-1</sup>	reciprocal mole per liter J • K per pascal
J • mol <sup>-1</sup> • K <sup>-1</sup>	joule per mole per kelvin	(mol • L <sup>-1</sup> ) <sup>-1</sup> • Pa <sup>-1</sup> • s <sup>-1</sup>	reciprocal mole per liter per pascal per second
J • s	joule second	(mol • L <sup>-1</sup> ) <sup>-1</sup> • cm <sup>-1</sup>	reciprocal mole per liter per centimeter
K	kelvin	(mol • L <sup>-1</sup> ) <sup>-1</sup> • s <sup>-1</sup>	reciprocal mole per liter per second
kg	kilogram	(mol • L <sup>-1</sup> ) <sup>-2</sup> • s <sup>-1</sup>	reciprocal mole per liter squared per second
kJ	kilojoule		
kJ • mol <sup>-1</sup>	kilojoule per mole		
kJ • V <sup>-1</sup> • equiv <sup>-1</sup>	kilojoule per volt per equivalent weight	nm	nanometer
kPa	kilopascal	Pa	pascal
L	liter	pct	percent
m	molality (moles solute per kilogram water)	ppm	part per million
M	molarity (moles solute per liter solution)	s	second
M <sup>-1</sup> • s <sup>-1</sup>	reciprocal mole per liter per second	s <sup>-1</sup>	reciprocal second
M <sup>-2</sup> • s <sup>-1</sup>	reciprocal mole per liter squared per second	s <sup>-1</sup> • K <sup>-1</sup>	reciprocal second per kelvin
m • s <sup>-1</sup>	meter per second	V	volt
		μm	micrometer
		°C	degree Celsius

### U.S. Customary

atm	atmosphere	tr oz/st	troy ounce per short ton
°F	degree Fahrenheit		



## SYMBOLS USED IN THIS REPORT

a	activity	N°	Avogadro's number, $6.02 \times 10^{23} \text{ mol}^{-1}$
A	absorbance	pH	$-\log (\text{activity of } \text{H}^+)$
c	concentration	pK	$-\log (\text{equilibrium constant})$
c	speed of light, $2.998 \times 10^8 \text{ m}\cdot\text{s}^{-1}$	pL	$-\log (\text{total activity of free ligand species})$
e <sup>-</sup>	electron	pM	$-\log (\text{total activity of all dissolved metal species})$
E	reduction potential; energy	R	gas constant, $8.3145 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ; reactant (reagent) concentration
E°	standard reduction potential	s	stoichiometric coefficient
Eh	reduction potential relative to the standard $\text{H}^+/\text{H}_2$ electrode	S°	standard entropy
F	Faraday constant, $96.485 \text{ kJ}\cdot\text{V}^{-1}\cdot\text{equiv}^{-1}$	t	time
h	Planck's constant, $6.626076 \times 10^{-34} \text{ J}\cdot\text{s}$	T	temperature
I	transmitted light intensity; ionic strength	T	light transmitted
I <sub>0</sub>	incident light intensity	v	frequency
k	wave number; rate constant	Z	reactant (substrate)
k'	Boltzmann's constant, $1.38066 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}$	β	cumulative equilibria
K	equilibrium constant	γ	activity coefficient
K <sub>a</sub>	acidity constant	ε	molar absorptivity
K <sub>c</sub>	concentration equilibrium constant	ΔE*	activation energy
l	length	ΔH*	enthalpy of activation
L	ligand	ΔS*	entropy of activation
L	wavelength	Δ <sub>f</sub> G°	standard Gibbs energy of formation
M	metal ion	Δ <sub>f</sub> H°	standard enthalpy of formation
n	number	Δ <sub>f</sub> S°	standard entropy of formation







# CYANIDE CHEMISTRY PRECIOUS METALS PROCESSING AND WASTE TREATMENT

By Charles M. Flynn, Jr., <sup>1</sup> and Sandra McGill Haslem<sup>2</sup>

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## ABSTRACT

This U.S. Bureau of Mines publication is a compilation of fundamental cyanide chemistry data obtained through an extensive review of the scientific literature. It includes information on thermodynamics and chemical equilibria, ultraviolet-visible and infrared spectra, and the chemistry and photochemistry of cyanide, chemical species derived from cyanide, and metal cyanide species. It also includes guidance on the use of the data for solving practical problems in precious metals applications.

This publication is intended mainly for use as a reference by personnel in the precious metals industry and regulatory agencies, and other cyanide users, to provide comprehensive information on cyanide chemistry. The document should assist in the formulation of effective policies for cyanide control in the construction, operation, and closure phases of precious metals mining and metallurgical operations. In addition, the data in this publication will be useful in other contexts, such as dealing with industrial cyanide usage, cyanide-containing wastes, and associated environmental problems.

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## CHAPTER 1.—GENERAL INTRODUCTION

### INTRODUCTION

Cyanide is used widely in industrial processes, including flotation, extractive metallurgy, electroplating, metal cleaning and finishing, pesticide manufacturing, photography, and steel manufacturing. In the precious metals industry, cyanide has been used for a century to extract gold and silver from ore. The cyanidation process is very efficient, being capable of extracting gold from ores as low in grade as 0.01 tr oz/st with over 90-pct efficiency; the recovery of gold from pregnant solutions is equally efficient (1-2).<sup>1</sup>

Cyanidation extraction processes differ depending on the type of ore being processed. Consequently, a variety of cyanide complexes of accessory elements in addition to gold and silver cyanide complexes are present during and after processing. Wastes produced from these operations include piles of spent ore from heap leaching and tailings ponds from ores processed in mills. Large variations in ore properties and treatment methods complicate the investigation of the fate of cyanide from these operations (1-10).

Cyanide from these wastes can cause environmental problems because of its toxicity. A thorough understanding of the transport and fate of cyanide in the environment is necessary because the toxicity of cyanide to different organisms varies with the chemical form of the cyanide. The chemical form of the cyanide depends on pH, exposure to light and air, and the presence and chemical forms of metals, e.g. Zn, Cu, and Fe. The transport of these species depends on solubilities, adsorption on materials such as soils and clays, and interactions with biomass. Much research has been published on the toxicity of cyanide, especially cyanide in natural waters (3, 8-10). Because cyanide complexes of different metals commonly occur in precious metals processing wastes, and because the chemical properties of the metal cyanide complexes differ greatly, the toxicity of cyanide varies tremendously depending on the extent to which it is complexed with metals.

### PURPOSE OF THIS PUBLICATION

An adequate understanding of the transport and fate of cyanide in the environment and the toxicity of cyanide as a function of its chemical form requires fundamental data on the chemistry of cyanide, species derived from cyanide, and metal cyanide complexes. The pertinent data compiled in this publication are summarized in the next section.

<sup>1</sup>Italic numbers in parentheses refer to items in the list of references at the end of this chapter.

This publication is intended mainly for use as a reference by personnel in the precious metals industry, and regulatory agencies, and other cyanide users, to provide comprehensive information on cyanide chemistry in order to assist in the formulation of effective policies for cyanide control in the construction, operation, and closure phases of mining and metallurgical operations. Beyond the field of mining and extractive metallurgy of precious metals, the data in this publication will be useful in dealing with industrial cyanide usage, cyanide-containing wastes, and associated environmental problems.

### CONTENT AND ORGANIZATION OF THIS PUBLICATION

The required fundamental data include thermodynamics and chemical equilibria, ultraviolet-visible and infrared spectra, and the chemistry and photochemistry of cyanide, chemical species derived from cyanide, and metal cyanide chemical species. This publication is a compilation of such data obtained via an extensive review of the literature. Guidance on the use of the data for solving practical problems related to precious metals processing is also included. The following paragraphs summarize the importance of these data and the organization of this publication.

Chapter 2 provides information on the nomenclature of chemical species, which is important in order to avoid confusion among the large number of chemical species mentioned in this publication. For metal complexes, modern nomenclature is emphasized and used because older nomenclature can be confusing.

Chapter 3 surveys the cyanides of the elements to show the extent to which the elements form cyanide species important in mining and extractive metallurgy.

Thermodynamic data define the chemical equilibria of cyanide and its metal complexes and the dependence of those equilibria on pH, redox potential, ionic strength, and the presence of different metal compounds. The pertinent thermodynamic theory and equations, the sources and accuracy of the thermodynamic and equilibrium data, and the presentation of equilibrium data in diagrams are described in chapter 4 and appendix A. The data and diagrams are compiled in appendixes B, C, D, and E. As described in chapter 4, many publications that contain thermodynamic and equilibrium data and diagrams for hydrometallurgy are not fully reliable because obsolete data were used. For this publication, much effort was given to obtaining the most recent and reliable data.

The absorption of light by cyanide, chemical species derived from cyanide, metal cyanide species, and other chemical species is important in connection with the fate of these species in the environment and in artificial



cyanide destruction processes. This is particularly important for certain metal cyanide complexes, particularly those of iron. For these reasons, pertinent data on ultraviolet-visible spectra are compiled in chapter 5. Ultraviolet-visible spectra are also useful for the detection and identification of metal cyanide species.

Infrared spectra are useful for identification of free cyanide and derived species such as cyanate and thiocyanate, and metal cyanide complexes. Pertinent infrared spectral data are compiled in chapter 6.

The extent to which chemical equilibria prevail depends on chemical reaction rates. Chemical reaction rates (chemical kinetics) are as important as thermodynamics in determining the fate of cyanide, species derived therefrom, and metal cyanide species in the environment, and the destruction or recovery of cyanide in industrial processes. Slow reaction rates are often encountered in reactions involving oxygen, slightly soluble solids, or the cyanide complexes of certain metals, notably iron. The rates of chemical reactions depend on solution composition, pH, temperature, and the presence of light when light-absorbing substances are involved.

Cyanide undergoes reactions with different oxidants, which are of interest for cyanide's environmental degradation or artificial destruction. Cyanide and the chemical species formed via its oxidation react with water and accessory chemical species such as ammonia and sulfide. All of the chemical species thus formed are eventually converted to carbon oxide species. The rates of these reactions, which differ greatly, are described in chapter 7, with additional data compiled in appendix F.

The chemistry of metal cyanide species is very important with regard to the environmental behavior of cyanide and industrial processes involving cyanide. Cyanide is a very strong complexing agent, and more often than not it may be present as dissolved metal complexes or slightly soluble metal compounds. Metal cyanide species differ greatly in their reactivities with regard to liberation or oxidation of the complexed cyanide. The chemistry of the cyanide species of individual metals is described in chapter 8.

The cyanide complexes of some metals absorb visible and ultraviolet light. This fact is particularly important for certain metal cyanide complexes, notably those of iron, cobalt, and chromium, which are unreactive toward reagents such as acids and oxidants that destroy other metal cyanide species. The absorption of light by the cyanide complexes of iron, cobalt, and chromium results in photochemical reactions that destroy the complexes. These photochemical reactions are important for the environmental degradation of iron, cobalt, and chromium cyanide complexes, and can be utilized with oxidants for their industrial destruction. Chapter 9 describes the photochemical reactions of metal cyanide complexes applicable to their degradation and destruction.

Metal cyanide complexes usually react with other heavy-metal salts or cations to form slightly soluble compounds. This often occurs when metal-containing cyanide solutions become depleted in cyanide, e.g., during treatment with oxidants to destroy cyanide. Metal cyanide complexes may also be deliberately removed from solution by addition of metal compounds such as iron salts. Chapter 10 describes the reactions between different metal cyanide species and other metal compounds, in particular iron salts.

The use of the data in this publication may not appear straightforward to all users. Chapter 11 provides several illustrations of the use of equilibrium predominance area diagrams or thermodynamic data for the solution of practical problems. Chapter 12 serves a similar purpose with regard to reaction rate problems.

Terminology is introduced, defined, and used in the chapters where needed. To further facilitate the use of this publication, definitions of terms are listed in a glossary, which follows chapter 12.

The illustrations and tables in this publication are numbered by chapter or appendix. For example, figure 7-1 is figure 1 in chapter 7, and table D-10 is table 10 in appendix D. References for the sources of data are given at the ends of the respective chapters or appendices.

There is need for much additional research on the chemical reactions of cyanide, species derived from cyanide, and metal cyanide species. The gaps in current knowledge are evident from the discussions and data in the respective chapters.

## DATA NOT INCLUDED IN THIS PUBLICATION

Data on the toxicity, biochemistry, and environmental behavior (beyond fundamental chemistry) of cyanides, analytical procedures for cyanides, and the engineering details of industrial processes are not included in this publication. Information on the toxicity, biochemistry, and environmental behavior of cyanides is available in several sources (3, 8-10). Sources of mining and metallurgical process and waste treatment information are cited above (1-7). Information on the practical analytical chemistry of cyanide and metal cyanide species has been compiled elsewhere (3, 11-13).

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## CHAPTER 2.—NOMENCLATURE

### INTRODUCTION

This chapter discusses nomenclature for chemical species of interest in cyanide chemistry. Nomenclature is important because many chemical species have more than one name, which can cause confusion. Causes of multiple names include (1) historical precedent versus modern systematic nomenclature, (2) industrial practice versus nomenclature derived from fundamental principles, (3) different systems of nomenclature, (4) discovery of new chemical species for which older nomenclature is inadequate, (5) the exponential growth of chemical information since World War II, and (6) nomenclature changes in the indexes of Chemical Abstracts (1-8).<sup>1</sup> Modern chemical nomenclature is based on a systematic hierarchy of rules compiled by the International Union of Pure and Applied Chemistry (IUPAC) (9). The indexes of Chemical Abstracts do not always follow the IUPAC rules; sometimes the more familiar historical or industrial names are used. Chemical species names used historically or in industrial practice are often short, well known, and easily remembered. However, they are rarely systematic. The systematically derived names of IUPAC nomenclature can be unwieldy, but their use may cause less confusion.

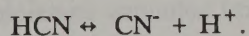
This chapter outlines nomenclature for forms of cyanide, species derived from cyanide, and other chemical species that may exist in cyanide process streams. The formulas and names of species derived from cyanide are tabulated, and nomenclature for metal species is discussed.

As a rule, modern nomenclature is adopted in this publication. This use will serve to familiarize readers with it; modern nomenclature is also preferred because of the quantity and variety of chemical data compiled in this publication.

### FORMS OF CYANIDE

#### Free Cyanide

Free cyanide is uncomplexed cyanide ion,  $\text{CN}^-$ , and molecular hydrogen cyanide,  $\text{HCN}$  (10). They are related by the acid dissociation of  $\text{HCN}$ :



The concentration of free cyanide is the sum of the  $\text{CN}^-$  and  $\text{HCN}$  concentrations, as illustrated in the equilibrium distribution diagram shown in figure 2-1. Figure 2-1 shows the proportions of free cyanide in the  $\text{CN}^-$  and  $\text{HCN}$  forms

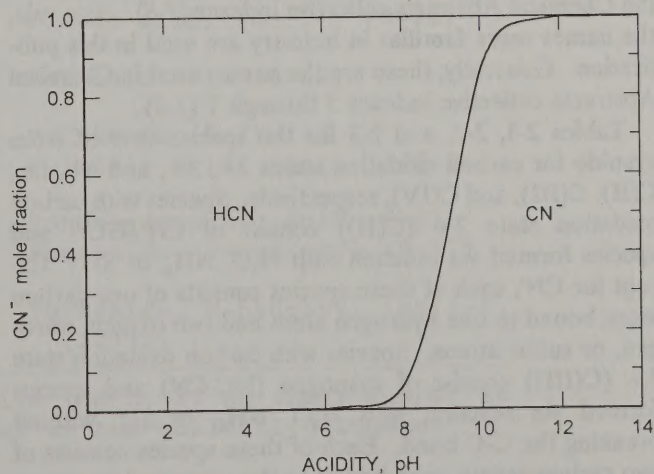
as a function of pH at 25° C and zero ionic strength. At pH above 9.2  $\text{CN}^-$  predominates, and at pH below 9.2  $\text{HCN}$  predominates. This equilibrium is discussed as an example in chapter 4.

### Complexed Cyanide

Cyanide bound to metal ions is referred to as "complexed" cyanide (10). Complexed cyanide may occur as solids  $\text{M}(\text{CN})_q(\text{s})$  or dissolved species  $[\text{M}(\text{CN})_p]^{q-p}(\text{aq})$ , where  $\text{M}^{q+}$  represents any metal ion of charge or oxidation state  $q+$ . The strength of the  $\text{M-CN}$  bonds in complexed cyanides depends on the metal and the  $\text{CN}: \text{M}$  mole ratio. The  $\text{M-CN}$  bond strength is correlated with the equilibrium constant for the formation of the species. The equilibria of some metal cyanides are discussed as examples in chapter 4. A general survey of cyanides of the elements is presented in chapter 3.

Metal cyanide complexes have been classified into two groups in regard to their reactivity with acids (10). The first group of metal cyanide complexes are rapidly and completely decomposed by acids, with all complexed  $\text{CN}^-$  converted to  $\text{HCN}$ . These cyanide complexes are termed "weak-acid-dissociable" (WAD). Examples are the cyanide complexes of Zn, Cd, and Ni. The second group of metal cyanide complexes are resistant to decomposition by acids. These cyanide complexes are termed "non-WAD" cyanide complexes. Examples are the cyanide complexes of cobalt and iron. This classification is in reality too simple, because there are some metal cyanide complexes that are only partially decomposed by acids. For these metals,

Figure 2-1



Equilibrium distribution diagram for free cyanide versus pH at 25° C and zero ionic strength.

<sup>1</sup>Italic numbers in parentheses refer to items in the list of references at the end of this chapter.



complete decomposition of their cyanide complexes by acids requires the addition of a complexing agent, precipitant, or oxidant. This group may be termed "partially WAD" cyanide complexes. Examples of partially WAD metal cyanide complexes are those of Cu, Ag, Au, and Hg.

Both thermodynamic and kinetic factors determine how readily metal cyanide complexes are decomposed by acids. These factors are discussed in detail in chapter 8. The equilibria of WAD cyanide complexes are usually rapidly established, which determines the chemical behavior of these complexes. These equilibria are presented as diagrams, discussed in chapter 4 and shown in appendix E. The equilibrium data for metal cyanide and other species from which these diagrams are generated are compiled in appendix D.

### SPECIES DERIVED FROM CYANIDE

A considerable number of other chemical species are derived from  $\text{CN}^-$ . These species form via oxidation or reaction with  $\text{H}_2\text{O}$  or other species. Other species that can react with  $\text{CN}^-$  or derived species are ammonia ( $\text{NH}_3$ ), hydrogen sulfide ( $\text{SH}^-$ ), and certain other sulfur species. Any of these species could form via reactions of  $\text{CN}^-$  or derived species under appropriate conditions. The large number of conceivable species that are products of all of these reactions have been compiled and systematized as described below. There appears to be no other recent compilation of the nomenclature and chemistry of  $\text{CN}^-$  and derived species. The reactions that are known or expected to occur and an assessment of which species are important in precious metals mining and closure operations are discussed in chapter 7.

The formulas, names, and Chemical Abstracts Service (CAS) registry numbers of  $\text{CN}^-$  and derived species are shown in tables 2-1 through 2-3. In many cases more than one name is included because of nomenclature changes in the Chemical Abstracts collective indexes (1-8). As a rule, the names more familiar in industry are used in this publication. Generally, these are the names used in Chemical Abstracts collective indexes 5 through 7 (1-3).

Tables 2-1, 2-2, and 2-3 list the species derived from cyanide for carbon oxidation states 2+, 3+, and 4+, i.e., C(II), C(III), and C(IV), respectively. Species with carbon oxidation state 2+ (C(II)) consist of  $\text{CN}^-/\text{HCN}$  and species formed via reaction with  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , or  $\text{SH}^-$ . Except for  $\text{CN}^-$ , each of these species consists of one carbon atom bound to one hydrogen atom and two oxygen, nitrogen, or sulfur atoms. Species with carbon oxidation state 3+ (C(III)) consist of cyanogen ( $\text{NC-CN}$ ) and species formed via reaction with  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , or  $\text{SH}^-$  without breaking the C-C bond. Each of these species consists of two carbon atoms, each bound to the other and to one or two oxygen, nitrogen, or sulfur atoms. Species with carbon oxidation state 4+ (C(IV)) consist of cyanogen chloride

( $\text{ClCN}$ ) and species formed via reaction with  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , or  $\text{SH}^-$ . Each of these species consists of one carbon atom bound to two or three oxygen, nitrogen, or sulfur atoms.

In tables 2-1 through 2-3, the species are arranged by chemical formula. The species are arranged according to increasing number of atoms bound to the carbon atom, then increasing number of oxygen atoms bound to the carbon atom. Abbreviated formulas are also given, which are used in chapter 7. The abbreviated formulas are enclosed in curly brackets, and only the carbon atoms and the atoms bound to the carbon atoms are shown. Species related by gain or loss of  $\text{H}^+$  are collectively given one abbreviated formula. For example, oxalic acid and its anions,  $\text{H}_2\text{C}_2\text{O}_4$ ,  $\text{HC}_2\text{O}_4^-$ , and  $\text{C}_2\text{O}_4^{2-}$  are collectively given the abbreviated formula  $\{\text{OCCCCO}\}$ . Abbreviated formulas are not used for  $\text{ClCN}$ ,  $\text{NCO}^-$  (cyanate), and  $\text{SCN}^-$  (thiocyanate).

The chemical formulas are written to reflect the molecular structures of the species. This is necessary to avoid confusion, because of the existence of isomers. Isomers are species that have the same composition in terms of numbers of atoms and ionic charges, but different molecular structures. Examples of isomers are cyanate and fulminate. Cyanate is often written  $\text{CNO}^-$  in the metallurgical literature. This creates confusion with fulminate, which is also  $\text{CNO}^-$ , but with a different structure. Experimentally determined molecular structures show the following: Cyanate is  $\text{NCO}^-$  or  $\text{OCN}^-$ , a species with a linear molecular structure, with the carbon atom in the middle. Fulminate is  $\text{CNO}^-$  or  $\text{ONC}^-$ , also a species with a linear molecular structure, with the nitrogen atom in the middle (11). Consequently, in this report, cyanate will be written  $\text{NCO}^-$ , and fulminate  $\text{CNO}^-$ . Similarly, thiocyanate is  $\text{SCN}^-$  or  $\text{NCS}^-$  (not  $\text{CNS}^-$ ; the carbon atom is in the middle) (11). (The sulfur analog of fulminate,  $\text{CNS}^-$ , with the nitrogen atom in the middle, is unknown.)

Fulminic acid ( $\text{HCNO}$ ) and fulminate ion ( $\text{CNO}^-$ ) can be thought of as derived from  $\text{CN}^-$  by oxidation at the nitrogen atom, and formohydroxamic acid ( $\text{H-CO-NH-OH}$ ) by subsequent reaction with  $\text{H}_2\text{O}$ . These species, which contain carbon in the 2+ oxidation state, are listed at the end of table 2-1. Abbreviated formulas are not used for these species. (The silver or gold salts of the fulminate ion  $\text{CNO}^-$  are not to be confused with "fulminating silver" or "fulminating gold" in the literature. The latter two materials are silver or gold nitride compounds formed in alkaline ammoniacal solutions containing silver or gold (12).)

The arrangement of data for cyanide and derived species in tables 2-1 through 2-3 is incorporated in chapters 5 and 7 and appendixes B and C.

Cyanide and many of the derived species are known to undergo condensation reactions (e.g., cyanamide to cyanoguanidine or melamine). Such condensation products are usually encountered only at high concentrations and are consequently not considered in this publication.



Table 2-1.-Nomenclature of carbon(II) species  
derived from cyanide

Formula and abbreviation	CAS <sup>1</sup> registry number	Name, followed by numbers of <u>Chemical Abstracts</u> collective indexes in parentheses
HCN {HCN}	74-90-8	Hydrocyanic acid (5-12)
CN <sup>-</sup> {HCN}	57-12-5	Cyanide (5-12)
H-C(NH)(NH <sub>2</sub> ) {HCNN}	463-52-5	Formamidine (5-8) Methanimidamide (9-12)
H-C(NH <sub>2</sub> ) <sub>2</sub> <sup>+</sup> {HCNN}	50676-76-1	Methanimidamide, conjugate monoacid (9-12)
H-CS-NH <sub>2</sub> {HCSN}	115-08-2	Formamide, thio- (5-8) Methanethioamide (9-12)
H-CS-SH {HCSS}	4472-10-0	Formic acid, dithio- (5-7) Methanedithioic acid (8-12)
H-CS <sub>2</sub> <sup>-</sup> {HCSS}	37619-02-6	Methane(dithioic) acid, ion(1-) (9-12)
H-CO-NH <sub>2</sub> {HCON}	75-12-7	Formamide (5-12)
H-CO-SH {HCOS}	16890-80-5	Formic acid, thio (5-8) Methanethioic acid (9-12)
H-COS <sup>-</sup> {HCOS}	37691-01-5	Methanethioic acid, ion(1-) (9-12)
H-CO-OH {HCOO}	64-18-6	Formic acid (5-12)
H-CO <sub>2</sub> <sup>-</sup> {HCOO}	71-47-6	Formates (5-7) Formic acid, ion(1-) (8-12)
HCNO	506-85-4	Fulminic acid (5-12)
CNO <sup>-</sup>	28269-67-2	Fulminate (5-7) Fulminic acid, ion(1-) (8-9)
H-CO-NH-OH	4312-87-2	Formohydroxamic acid (5-8) Formamide, N-hydroxy- (9-12)
H-CO-NH-O <sup>-</sup>	78204-40-7	Formamide, N-hydroxy, ion(1-) (10-11)

<sup>1</sup>CAS Chemical Abstracts collective index; if no index number is given, the compound does not appear in the collective indexes.



Table 2-2.-Nomenclature of carbon(III) species  
derived from cyanide

Formula and abbreviation	CAS <sup>1</sup> registry number	Name, followed by numbers of <u>Chemical Abstracts</u> collective indexes in parentheses
NC-CN {NCCN}	460-19-5	Cyanogen (5-8) Ethanedinitrile (9-12)
NC-C(NH)-NH <sub>2</sub> {NCCNN}	37507-70-3	Formamide, 1-cyano (5-6) Carbonocyanidimidic amide (9-12)
NC-CS-NH <sub>2</sub> {NCCSN}	471-24-9	Formamide, 1-cyanothio- (6-8) Carbonocyanidothioic amide (9-12)
NC-CS-SH {NCCSS}	38093-84-4	Formic acid, cyanodithio- (5-8) Carbonocyanidodithioic acid (9-12)
NC-CS <sub>2</sub> <sup>-</sup> {NCCSS}	44201-42-5	Carbonocyanidodithioic acid, ion(1-) (9)
NC-CO-NH <sub>2</sub> {NCCON}	4370-12-1	Formamide, 1-cyano- (6-7) Carbonocyanidic amide (9-12)
NC-CO-SH {NCCOS}	57550-98-8	Formic acid, 1-cyanothio- (7-8) Carbonocyanidothioic acid (9-12)
NC-COS <sup>-</sup> {NCCOS}	no entries	Carbonocyanidothioic acid, ion(1-)
NC-CO-OH {NCCOO}	19270-07-6	Formic acid, cyano (5-8) Carbonocyanidic acid (9-12)
NC-CO <sub>2</sub> <sup>-</sup> {NCCOO}	no entries	Carbonocyanidic acid, ion(1-)
H <sub>2</sub> N-C(NH)-C(NH)C- NH <sub>2</sub> {NNCCNN}	4013-33-6	Oxamidine (5-8) Ethanediimideamide (9-12)
(H <sub>2</sub> N) <sub>2</sub> C-C(NH <sub>2</sub> ) <sub>2</sub> <sup>2+</sup> {NNCCNN}	132724-41-5	1,2-Ethanediylum, 1,1,2,2- tetraamino- (12)
H <sub>2</sub> N-C(NH)-CS-NH <sub>2</sub> {NNCCSN}	no entries	Formamide, amidinothio- Ethanethioamide, aminoimino-
H <sub>2</sub> N-CS-CS-NH <sub>2</sub> {NSCCSN}	79-40-3	Oxamide, dithio- (5-8) Ethanedithioamide (9-12)



Table 2-2.-Nomenclature of carbon(III) species  
derived from cyanide-Continued

Formula and abbreviation	CAS <sup>1</sup> registry number	Name, followed by numbers of <u>Chemical Abstracts</u> collective indexes in parentheses
$\text{H}_2\text{N}-\text{C}(\text{NH})-\text{CS}-\text{SH}$ {NNCCSS}	no entries	Formic acid, amidinodithio- Ethane(dithioic) acid, amino- imino-
$\text{H}_2\text{N}-\text{C}(\text{NH})-\text{CS}_2^-$ {NNCCSS}	no entries	Ethane(dithioic) acid, amino- imino, ion(1-)
$\text{H}_2\text{N}-\text{CS}-\text{CS}-\text{SH}$ {NSCCSS}	no entries	Oxamic acid, trithio- Ethane(dithioic) acid, amino- thioxo-
$\text{H}_2\text{N}-\text{CS}-\text{CS}_2^-$ {NSCCSS}	no entries	Ethane(dithioic) acid, amino- thioxo, ion(1-)
$\text{HS}-\text{CS}-\text{CS}-\text{SH}$ {SSCCSS}	82766-65-2	Oxalic acid, tetrathio- Ethanebis(dithioic) acid (9-10, 12)
$\text{S}_2\text{C}-\text{CS}_2^{2-}$ {SSCCSS}	78906-82-8	Ethanebis(dithioic) acid, ion(2-) (10-12)
$\text{H}_2\text{N}-\text{C}(\text{NH})-\text{CO}-\text{NH}_2$ {NNCCON}	no entries	Formamide, amidino- Acetamide, 2-amino-2-imino-
$\text{H}_2\text{N}-\text{CS}-\text{CO}-\text{NH}_2$ {NSCCON}	16475-48-2	Oxamide, thio (6-8) Acetamide, 2-amino-2-thioxo- (9-10, 12)
$\text{H}_2\text{N}-\text{C}(\text{NH})-\text{CO}-\text{SH}$ {NNCCOS}	no entries	Formic acid, amidinothio- Ethanethioic acid, aminoimino-
$\text{H}_2\text{N}-\text{C}(\text{NH})-\text{COS}^-$ {NNCCOS}	no entries	Ethanethioic acid, amino- imino, ion(1-)
$\text{H}_2\text{N}-\text{CS}-\text{CO}-\text{SH}$ {NSCCOS}	no entries	Oxamic acid, 1,2-dithio- Ethanethioic acid, amino- thioxo-
$\text{H}_2\text{N}-\text{CS}-\text{COS}^-$ {NSCCOS}	no entries	Ethanethioic acid, amino- thioxo-, ion(1-)
$\text{H}_2\text{N}-\text{CO}-\text{CS}-\text{SH}$ {SSCCON}	97925-73-0	Oxamic acid, 1,1-dithio- (6-7) Ethane(dithioic) acid, amino- oxo- (10-11)
$\text{H}_2\text{N}-\text{CO}-\text{CS}_2^-$ {SSCCON}	no entries	Ethane(dithioic) acid, amino- oxo-, ion



Table 2-2.-Nomenclature of carbon(III) species  
derived from cyanide-Continued

Formula and abbreviation	CAS <sup>1</sup> registry number	Name, followed by numbers of <u>Chemical Abstracts</u> collective indexes in parentheses
HS-CS-CO-SH {SSCCOS}	no entries	Oxalic acid, trithio- Ethanethioic acid, mercapto- thioxo- (salt only) (9)
S <sub>2</sub> C-COS <sup>2-</sup> {SSCCOS}	no entries	Ethanethioic acid, mercapto- thioxo-, ion
H <sub>2</sub> N-CO-CO-NH <sub>2</sub> {NOCCON}	471-46-5	Oxamide (5-8) Ethanediamide (9-12)
H <sub>2</sub> N-C(NH)-CO-OH {NNCCOO}	27203-24-3	Formic acid, amidino- (7-8) Acetic acid, aminoimino- (9-11)
H <sub>2</sub> N-C(NH)-CO <sub>2</sub> <sup>-</sup> {NNCCOO}	no entries	Acetic acid, aminoimino- ion(1-)
H <sub>2</sub> N-CO-CO-SH (NOCCOS)	80487-41-8	Oxamic acid, 2-thio- (5-8) Ethanethioic acid, aminooxo- (9-11)
H <sub>2</sub> N-CO-COS <sup>-</sup> (NOCCOS)	no entries	Ethanethioic acid, aminooxo-, ion(1-)
H <sub>2</sub> N-CS-CO-OH {NSCCOO}	39894-60-5	Oxamic acid, 1-thio- Acetic acid, aminothioxo- (9-12)
H <sub>2</sub> N-CS-CO <sub>2</sub> <sup>-</sup> {NSCCOO}	no entries	Acetic acid, aminothioxo-, ion(1-)
HS-CO-CO-SH {SOCCOS}	17148-96-8	Oxalic acid, 1,2-dithio- (5-8) Ethanebis(thioic) acid (9-12)
SOC-COS <sup>2-</sup> {SOCCOS}	37183-16-7	Ethanebis(thioic) acid, ion(2-) (9-11)
HS-CS-CO-OH (SSCCOO)	64148-58-9	Oxalic acid, 1,1-dithio- Acetic acid, mercaptothioxo- (9) Formic acid, (dithiocarboxy)- (10-12)
S <sub>2</sub> C-CO <sub>2</sub> <sup>2-</sup> {SSCCOO}	65194-59-4	Formic acid, (dithiocarboxy)- ion(2-) (10)
H <sub>2</sub> N-CO-CO-OH {NOCCOO}	471-47-6	Oxamic acid (5-8) Acetic acid, aminooxo- (9-12)



Table 2-2.--Nomenclature of carbon(III) species  
derived from cyanide--Continued

Formula and abbreviation	CAS <sup>1</sup> registry number	Name, followed by numbers of <u>Chemical Abstracts</u> collective indexes in parentheses
$\text{H}_2\text{N}-\text{CO}-\text{CO}_2^-$ {NOCCOO}	598-90-3	Oxamate (5-7) Oxamic acid, ion(1-) (8) Acetic acid, aminooxo-, ion(1-)
$\text{HS}-\text{CO}-\text{CO}-\text{OH}$ {SOCCOO}	2689-56-7	Oxalic acid, thio- (5-8) Acetic acid, mercaptooxo- (9-10)
$\text{SOC}-\text{CO}_2^-$ {SOCCOO}	no entries	Acetic acid, mercaptooxo-, ion(2-)
$\text{HO}-\text{CO}-\text{CO}-\text{OH}$ {OCCOO}	144-62-7	Oxalic acid (5-8) Ethanedioic acid (9-12)
$\text{HO}-\text{CO}-\text{CO}_2^-$ {OCCOO}	920-52-5	Oxalic acid, ion(1-) (8) Ethanedioic acid, ion(2) (9-12)
$\text{O}_2\text{C}-\text{CO}_2^{2-}$ {OCCOO}	338-70-5	Oxalates (5-7) Oxalic acid, ion(2-) (8) Ethanedioic acid, ion(2-) (9-12)

<sup>1</sup>CAS Chemical Abstracts collective index; if no index number is given, the compound does not appear in the collective indexes.



Table 2-3.-Nomenclature of carbon(IV) species  
derived from cyanide

Formula and abbreviation	CAS <sup>1</sup> registry number	Name, followed by numbers of <u>Chemical Abstracts</u> collective indexes in parentheses
ClCN	506-77-4	Cyanogen chloride (5-12)
BrCN	506-68-3	Cyanogen bromide (5-12)
NC-NH <sub>2</sub> {CNN}	420-04-2	Cyanamide (5-12)
NCNH <sup>-</sup> {CNN}	67131-47-9	Cyanamide, ion(1-) (10-12)
CN <sub>2</sub> <sup>2-</sup> {CNN}	20328-93-2	Cyanamide, ion(2-) (8-12)
NCS <sup>-</sup>	302-04-5	Thiocyanate (5-7, 9-12) Thiocyanic acid, ion(1-) and Isothiocyanic acid, ion(1-) (8)
HNCO	420-05-3	Cyanic acid (5-12)
NCO <sup>-</sup>	661-20-1	Cyanate (5-7, 9-12) Cyanic acid, ion(1-) and Isocyanic acid, ion(1-) (8)
HNC(NH <sub>2</sub> ) <sub>2</sub> {CINN}	113-00-8	Guanidine (5-12)
C(NH <sub>2</sub> ) <sub>3</sub> <sup>+</sup> {CINN}	25215-10-5	Guanidine, conjugate monoacid (8-12)
SC(NH <sub>2</sub> ) <sub>2</sub> {CSNN}	62-56-6	Urea, thio- (5-8) Thiourea (9-12)
H <sub>2</sub> N-CS-SH {CSSN}	594-07-0	Carbamic acid, dithio- (5-8) Carbamodithioic acid (9-12)
H <sub>2</sub> N-CS <sub>2</sub> <sup>-</sup> {CSSN}	4384-82-1	Carbamic acid, dithio-, ion(1-) (8) Carbamodithioic acid, ion(1-) (9-12)
CS(SH) <sub>2</sub> {CSSS}	594-08-1	Carbonic acid, trithio- (5-8) Carbonotrithioic acid (9-12)
CS <sub>3</sub> <sup>2-</sup> {CSSS}	15644-49-2	Carbonic acid, trithio-, ion(2-) (8) Carbonotrithioate (9-12)
OC(NH <sub>2</sub> ) <sub>2</sub> {CONN}	57-13-6	Urea (5-12)



Table 2-3.-Nomenclature of carbon(IV) species  
derived from cyanide—Continued

Formula and abbreviation	CAS <sup>1</sup> registry number	Name, followed by numbers of <u>Chemical Abstracts</u> collective indexes in parentheses
$\text{H}_2\text{N}-\text{CO}-\text{SH}$ {COSN}	19045-66-0	Carbamic acid, thio- (5-8) Carbamothioic acid (9-12)
$\text{H}_2\text{N}-\text{COS}^-$ {COSN}	63294-87-1	Carbamothioic acid, ion(1-) (10)
$\text{CS}(\text{OH})(\text{SH})$ {COSS}	4741-30-4	Carbonic acid, dithio- (5-8) Carbonodithioic acid (9-12)
$\text{COS}_2^{2-}$ {COSS}	30981-29-4	Carbonic acid, dithio-, ion(1-) (8) Carbonodithioate (9-12)
$\text{H}_2\text{N}-\text{CO}-\text{OH}$ {COON}	463-77-4	Carbamic acid (5-12)
$\text{H}_2\text{N}-\text{CO}_2^-$ {COON}	302-11-4	Carbamic acid, ion(1-) (8-9, 11-12)
$\text{CO}(\text{OH})(\text{SH})$ {COOS}	10016-32-7	Carbonic acid, thio- (5-8) Carbonothioic acid (9-12)
$\text{CO}_2\text{S}^{2-}$ {COOS}	24389-08-0	Carbonic acid, thio-, ion(2-) (8) Carbonothioate (10-11)
$\text{CO}(\text{OH})_2$ {COOO}	463-79-6	Carbonic acid (5-12)
$\text{HO}-\text{CO}_2^-$ {COOO}	71-52-3	Carbonates, acid (5-7) Carbonate, hydrogen (8-12)
$\text{CO}_3^{2-}$ {COOO}	3812-32-6	Carbonates (5-7) Carbonate (8-12)

<sup>1</sup>CAS Chemical Abstracts collective index; if no index number is given, the compound does not appear in the collective indexes.



## AUXILIARY SPECIES

To describe the equilibria and reactions in situations where  $\text{CN}^-$  and metal cyanide complexes exist, all other chemical species that might participate must be included. These are referred to in this publication as "auxiliary" species. They include

1.  $\text{H}_2\text{O}$ ,  $\text{H}^+$ , and  $\text{OH}^-$ .
2. Uncomplexed metal ions.
3. Any other species that may precipitate or complex with metal ions, e.g.  $\text{S}^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{NH}_3$ , or  $\text{Cl}^-$ .
4. Other reagents, e.g., added oxidizing agents such as  $\text{H}_2\text{O}_2$  or  $\text{ClO}^-$ , and their reduction products.

Especially with WAD cyanide complexes, for which equilibria are usually established rapidly, the species that exist depend on pH and the presence of other species that may precipitate or complex with the metal ions. These equilibria are discussed in chapters 4 and 8, tabulated in appendix D, and diagramed in appendix E.

## METAL SPECIES

Insofar as the nomenclature for metal species in much metallurgical literature corresponds to that in the older chemical literature, some readers may not be familiar with modern chemical nomenclature, which is standardized and more systematic (9). This section will address oxidation states, metal complexes and complexing agents, and metal hydroxides.

The modern Roman numeral system for designating oxidation states is used here in preference to historically used suffixes such as "-ous" and "-ic" for cationic and neutral metal species. For anionic metal species, the suffix "ite" is abandoned, and the suffix "-ate" is used with the Roman numeral for the metal oxidation state. This practice is exemplified by metal cyanide complexes, e.g., dicyanoaurate(I) instead of aurocyanide or dicyanoaurite for  $[\text{Au}(\text{CN})_2]^{1-}$ , and hexacyanoferrate(II) and hexacyanoferrate(III) instead of ferrocyanide and ferricyanide for  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$ , respectively. This precise nomenclature is necessary because many metal ions form more than one cyanide complex, which makes the old nomenclature inadequate and confusing. For example, Cu(I) and cyanide form the species  $[\text{Cu}(\text{CN})_2]^{1-}$ ,  $[\text{Cu}(\text{CN})_3]^{2-}$ , and  $[\text{Cu}(\text{CN})_4]^{3-}$ , for which the respective names are dicyanocuprate(I), tricyanocuprate(I), and tetracyanocuprate(I).

Metals are often referred to in terms of particular oxidation states in a general context without specifying other details of the chemical composition or environment. In the older chemical literature and in much metallurgical literature, the symbol for the metal ion is commonly used in such situations, e.g.,  $\text{Fe}^{2+}$  for Fe in the 2+ oxidation

state. In the older systems, symbols such as  $\text{Fe}^{2+}$  are used to specify the uncomplexed ion. In modern nomenclature (9), metals in particular oxidation states without reference to chemical composition or environment are symbolized with the Roman numeral, e.g., Fe(II) for Fe in the 2+ oxidation state. This practice is followed throughout this publication.

The term "ligand" is used for any molecule or ion bound to a metal ion, whether it be  $\text{H}_2\text{O}$  or  $\text{OH}^-$  or any complexing agent. Abbreviations are often used for organic ligands. In modern nomenclature (9) it is customary to use lowercase letters enclosed in parentheses for such abbreviations. Examples include  $(\text{H}_4\text{edta})$  and  $(\text{edta})^{4-}$  for free ethylenediaminetetraacetic acid and the free ethylenediaminetetraacetate anion,  $[\text{Cu}(\text{edta})]^{2-}$  for ethylenediaminetetraacetatocuprate(II),  $[\text{Ni}(\text{en})_3]^{2+}$  for tris(ethylenediamine)nickel(II), and  $[\text{Fe}(\text{nta})_2]^-$  for bis(nitrilotriacetato)ferrate(III). For further details, the interested reader should consult the literature (9).

The nomenclature regarding precipitated metal "hydroxides" requires comment for three reasons. First, precipitated metal "hydroxides" hardly ever contain stoichiometric ratios of metal oxide to  $\text{H}_2\text{O}$ . Second, many metal oxides do not react with  $\text{H}_2\text{O}$  to form hydroxides. Third, modern techniques such as X-ray diffraction, neutron diffraction, infrared spectroscopy, and nuclear magnetic resonance spectroscopy enable the identification of  $\text{OH}^-$  groups in solids. Structurally, many precipitated metal "hydroxides" do not contain stoichiometric ratios of  $\text{OH}^-$  groups to metal atoms, and they should be termed "hydrous metal oxides." When the term "hydrous metal oxide" is appropriate rather than "metal hydroxide," it is used in this publication. This is the case for most heavy metals in oxidation state 3+ or higher.

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## CHAPTER 3.—SURVEY OF CYANIDES OF THE ELEMENTS

### INTRODUCTION

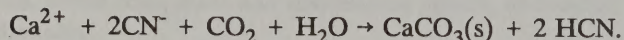
Precious metal ores often contain a variety of accessory elements. In mining and processing, many of the accessory elements can be leached, and transported through the process, where they report to liquid and solid wastes. The question arises as to what extent the accessory elements interact with  $CN^-$ . This chapter answers that question by presenting an overview of the cyanide chemistry of the elements. A summary of this overview is provided in figure 3-1. The following paragraphs survey the cyanide chemistry of the elements in each column of the periodic table.

### SURVEY OF CYANIDES OF THE ELEMENTS

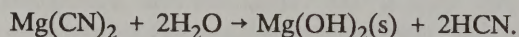
#### Alkali and Alkaline Earth Metals

The cyanides of the alkali metals Li, Na, K, Rb, and Cs (1)<sup>1</sup> are very soluble in water, with complete dissociation to alkali metal cations and free cyanide ion.

The cyanides of the heavier alkaline earths Ca, Sr, and Ba (2) are also water soluble and are completely dissociated to alkaline-earth metal cations and free cyanide ion. However, they are readily converted to HCN via reaction with  $CO_2$ , because of the insolubility of their carbonates; e.g.,



The cyanides of the lighter alkaline earths beryllium and magnesium (2) are even more readily hydrolyzed, also because of the low solubility of their hydroxides; e.g.,



#### Lanthanide and Actinide Metals

The cyanides of the lanthanides are poorly known. Cyanides of some lanthanide elements have been prepared, and they are decomposed by  $H_2O$  with liberation of HCN (3-4). No information was located for actinide metal cyanides. Like the lanthanide metal cyanides, they are expected to hydrolyze readily because of the insolubility of the metal hydroxides.

#### Transition Metals

Most of the transition metals form cyanide complexes of differing stabilities (3). As a rough general rule,

stabilities increase with atomic number along each of the three rows of transition metals in the periodic table. The cyanides of Ti, Zr, Hf, Nb, (Cb), and Ta are hardly known, but are expected to hydrolyze readily because of the insolubility of the hydrous metal oxides. Cyanide complexes of niobium in lower oxidation states are known, but they are readily oxidized and hydrolyzed (5).

Among the transition metals, iron is the most common cyanide-forming accessory element in connection with mining and extractive metallurgy. The metals Ni, Co, Mn, Cr and V are less common, but they all form cyanide complexes of differing stabilities. The chemistry of the cyanide complexes of these metals is described in detail in chapters 8, 9, and 10.

Cyanide complexes of Mo, W, and Re are well known, but none of them contain the metal in the highest oxidation state. Stable cyanide species are not known for Mo(V), W(V), or Re(VII). Cyanide complexes of Mo, W, and Re are not likely to be encountered in extractive metallurgy.

The cyanide complexes of the platinum-group metals are among the most stable of all known metal complexes; they are stable even in strongly acid solutions. They may conceivably form if platinum-group metals occur in gold-silver ores treated by cyanidation, but no such occurrences appear to have been reported. Very little is known about the equilibria and reactions of platinum-group metal cyanide species. Therefore they are not discussed in this publication.

#### Posttransition Metals

The posttransition metals Cu, Ag, Au, Zn, Cd, and Hg are all commercially important, and they all form binary cyanides and cyanide complexes (3). In the mining of precious metals, copper and zinc are the most likely accessory elements besides iron. The metals cadmium or mercury may also be encountered at some locations. The cyanide chemistry of all of these metals is described in detail in chapters 8 and 10.

#### Boron Group

The cyanides of B, Al, Ga, and In are all known or expected to be completely decomposed by water to oxide compounds and free cyanide (6-7). Indium may form cyanide complexes, judging by the use of cyanide baths for indium electroplating (8), but no fundamental data on indium cyanide complexes in solution exist. Thallium(I) forms  $TlCN$ , which like the alkali metal cyanides is water soluble and dissociates completely to  $Tl^+$  and free  $CN^-$  (9). Thallium(III) has recently been confirmed to form strong soluble cyanide complexes (10). Thallium(III) is expected

<sup>1</sup>Italic numbers in parentheses refer to items in the list of references at the end of this chapter.



Figure 3-1

## KEY

1H																	2He
S																	X
3Li	4Be											5B	6C	7N	8O	9F	10Ne
F	D											D	N	S	E	H	X
11Na	12Mg											13Al	14Si	15P	16S	17Cl	18Ar
F	D											D	D	N	E	H	X
19K	20Ca	21Sc	22Ti	23V	24Cr	25Mn	26Fe	27Co	28Ni	29Cu	30Zn	31Ga	32Ge	33As	34Se	35Br	36Kr
F	F	D	D	C	C	IC	IC	IC	IC	IC	IC	D	D	D	E	H	X
37Rb	38Sr	39Y	40Zr	41Nb	42Mo	43Tc	44Ru	45Rh	46Pd	47Ag	48Cd	49In	50Sn	51Sb	52Te	53I	54Xe
F	F	D	D	D	C	C	IC	IC	IC	IC	SC	D	D	D	N	H	X
55Cs	56Ba	57La	72Hf	73Ta	74W	75Re	76Os	77Ir	78Pt	79Au	80Hg	81Tl	82Pb	83Bi	84Po	85At	86Rn
F	F	D	D	d	C	C	IC	IC	IC	IC	SC	SC	I	D	X	X	X
87Fr	88Ra	89Ac															
X	F	X															

57La	58Ce	59Pr	60Nd	61Pm	62Sm	63Eu	64Gd	65Tb	66Dy	67Ho	68Er	69Tm	70Yb	71Lu
D	D	D	D	D	D	D	D	D	D	D	d	d	d	d
89Ac	90Th	91Pa	92U	93Np	94Pu	95Am	96Cm	97Bk	98Cf	99Es	100Fm	101Md	102No	103Lr
X	D	D	D	D	D	D	D	D	D	X	X	X	X	X

Survey of cyanides of the elements.



to be reduced to Tl(I) by  $\text{CN}^-$ , as shown by the thermodynamic data in tables B-1 and D-1. However, the rate of this reaction was reported to be slow (months) in acid solution; in alkaline solution with free  $\text{CN}^-$  present, the rate of the redox reaction may be faster (10). Thallium is rarely if ever reported as an accessory element in precious metals hydrometallurgy, so Tl(III) cyanide complexes may not be a significant problem. Thermodynamic data for thallium species are compiled in tables D-19 and D-20.

### Carbon Group

Carbon forms a variety of binary neutral and anionic cyanide compounds known as cyanocarbons (11); none of them are likely to be encountered in extractive metallurgy.

The cyanides of Si, Ge, and Sn are all known or expected to be completely decomposed by water to oxide compounds and free cyanide (7, 12). Lead(II) is reported to form a slightly soluble mixed hydroxide cyanide when Pb(II) salt solutions are treated with an alkali metal cyanide (13), or when  $\text{PbO} \cdot x\text{H}_2\text{O}$  is treated with HCN (14, p. 141). Cyanide complexes of Pb(II) in solution are probably weak; there is no reliable published information on them.

### Nitrogen Group

The most important cyanide compound of nitrogen is the well-known cyanamide,  $\text{H}_2\text{NCN}$ . The chemistry of  $\text{H}_2\text{NCN}$  is described in chapter 7 in connection with oxidation products of cyanide. Dicyanamide,  $\text{HN}(\text{CN})_2$  (15), is not important metallurgically. Tricyanamide,  $\text{N}(\text{CN})_3$ , is unknown.

The cyanides of P, As, Sb, and Bi are all known or expected to be completely decomposed by water to oxide compounds and free cyanide (12; 14, p. 427).

### Oxygen Group

The sole cyanide compound of oxygen of interest is the well-known cyanate ion,  $\text{NCO}^-$ , which is the major oxidation product of cyanide. The formation of  $\text{NCO}^-$  in oxidation reactions of cyanide and its hydrolysis and further oxidation are described in chapter 7.

The most important sulfur cyanide species is the well-known thiocyanate ion,  $\text{SCN}^-$ . Other sulfur cyanide species exist, but they are all decomposed by water to give  $\text{SCN}^-$ ,  $\text{CN}^-$  or  $\text{HCN}$ , and  $\text{NCO}^-$  (14, pp. 916-917). The formation of  $\text{SCN}^-$  from cyanide and sulfur species and the oxidation of  $\text{SCN}^-$  are described in chapter 7.

Selenium forms selenocyanate ion,  $\text{SeCN}^-$ , by dissolution of elemental selenium in cyanide solutions. It is readily decomposed by acids, with liberation of free cyanide (14,

p. 967). Tellurium does not form stable cyanide species, e.g.,  $\text{TeCN}^-$ , in aqueous solutions (18).

### Halogen Group

The halogens all form the well-known cyanogen halides, e.g., cyanogen chloride,  $\text{ClCN}$ . These compounds are all hydrolyzed by water to halide and  $\text{NCO}^-$  ions. The formation of  $\text{ClCN}$  from cyanide and chlorinating agents and its hydrolysis are described in chapter 7.

### Rare Gas Group

The rare gases He, Ne, Ar, Kr, and Xe do not form cyanides.

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## CHAPTER 4.—CHEMICAL EQUILIBRIA

### INTRODUCTION

The extent to which a chemical reaction proceeds is determined by thermodynamics and kinetics. Thermodynamics determines how far a chemical reaction can proceed, by means of the standard Gibbs energy change for the reaction. Kinetics determines the rate at which the reaction proceeds. The role of kinetics is described in chapter 7 in the context of reactions of free  $\text{CN}^\cdot$  and derived species. This chapter outlines the pertinent thermodynamic theory and equations, discusses thermodynamic data requirements and sources, and describes graphical methodology for presenting equilibrium information. It concludes with examples showing how information on equilibria can be obtained by inspection of log K data.

### FUNDAMENTAL THERMODYNAMIC EQUATIONS

This section presents an outline of pertinent thermodynamic equations. For further details, the interested reader is referred to any of several standard texts on thermodynamics. The equations presented in this section are provided to assist the reader in doing calculations with the data in appendixes B, C, and D.

#### Individual Species

All thermodynamic data are relative to a standard state. The data of interest here are the standard enthalpy of formation  $\Delta_f H^\circ$ , standard Gibbs energy of formation  $\Delta_f G^\circ$ , and standard entropy  $S^\circ$ . For pure solid or liquid substances, the standard state is the form that is stable at the temperature of interest and a pressure of  $10^5$  Pa (1 bar or 750.06 mm Hg or  $(1/1.01325)$  atm). The standard temperature for tables of  $\Delta_f H^\circ$ ,  $\Delta_f G^\circ$ , and  $S^\circ$  of chemical species is  $25.00^\circ\text{C}$  ( $298.15\text{ K}$  or  $77.00^\circ\text{F}$ ). If the species is gaseous, the standard state is the ideal gas at a pressure of  $10^5$  Pa. The definition of the standard state for aqueous dissolved species is discussed below in connection with activity coefficients.

In the older data tables, the standard pressure is 1 atm. The change in standard pressure entails small changes in  $S^\circ$  and  $\Delta_f G^\circ$  values where gaseous species are involved. For most purposes, these changes are inconsequential. For example,  $S^\circ$  for a gas species is changed by  $R$  (gas constant)  $\ln(1/1.01325) = -0.1094\text{ J}\cdot\text{K}^{-1}$  at  $25^\circ\text{C}$ . The corresponding change in  $\Delta_f G^\circ$  values is  $RT$  (gas constant times absolute temperature)  $\ln(1/1.01325) = -0.0326\text{ kJ}$  at  $25^\circ\text{C}$ , per mole of gas species in the formation reaction.

The standard Gibbs energies of formation  $\Delta_f G^\circ$ , standard enthalpies of formation  $\Delta_f H^\circ$ , and standard entropies

of formation  $\Delta_f S^\circ$  of a chemical species are related as follows:

$$\Delta_f G^\circ = \Delta_f H^\circ - T \Delta_f S^\circ. \quad (4-1)$$

where  $T$  = absolute temperature,

and  $\Delta_f S^\circ$  = standard entropy of formation, which is given by

$$\Delta_f S^\circ = S^\circ_{\text{species}} - \sum_i s_i S^\circ_i, \quad (4-2)$$

where  $S^\circ_{\text{species}}$  = standard entropy of species in equation 4-1,

$S^\circ_i$  = standard entropies of  $i$  elements contained in the species,

and  $s_i$  = stoichiometric coefficients for formation of the species from the  $i$  elements.

### Chemical Reactions

For a chemical reaction,

$$\sum_i s_{r,i} (\text{reactant species})_{r,i} \rightarrow \sum_i s_{p,i} (\text{product species})_{p,i}, \quad (4-3)$$

$$\Delta_r G^\circ = \sum_i s_{p,i} (\Delta_f G^\circ)_{p,i} - \sum_i s_{r,i} (\Delta_f G^\circ)_{r,i}, \quad (4-4)$$

$$\Delta_r H^\circ = \sum_i s_{p,i} (\Delta_f H^\circ)_{p,i} - \sum_i s_{r,i} (\Delta_f H^\circ)_{r,i}, \quad (4-5)$$

$$\Delta_r S^\circ = \sum_i s_{p,i} (S^\circ)_{p,i} - \sum_i s_{r,i} (S^\circ)_{r,i}. \quad (4-6)$$

In equations 4-3 through 4-6, the  $s_{p,i}$  and  $s_{r,i}$  are the stoichiometric coefficients for the products and reactants, respectively, in the reaction; the Gibbs energy, enthalpy, and entropy terms have corresponding meanings.

The thermodynamic equilibrium constant  $K$  is defined by

$$\Delta_r G^\circ = -RT \ln K \quad (4-7)$$

$$= -2.3026 RT \log K \quad (4-8)$$

$$= -5.708 \log K \text{ at } 25^\circ\text{C}, \quad (4-9)$$



where  $T$  = absolute temperature,

and  $R$  = the gas constant,  $8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ .

The thermodynamic equilibrium constant  $K$  is related to the activities of the reactants and products by the mass-action equation

$$K = \frac{\prod_i (a^s)_{p,i}}{\prod_i (a^s)_{r,i}} \quad (4-10)$$

In logarithmic form,

$$\log K = \sum_i s_{p,i} \log a_{p,i} - \sum_i s_{r,i} \log a_{r,i} \quad (4-11)$$

where  $a_{p,i}$  and  $a_{r,i}$  = activities of the  $i$ th product and reactant species, respectively.

For gaseous species, fugacity is used instead of activity. Under conditions encountered in hydrometallurgy, gases can be considered ideal, so that fugacity is equal to partial pressure. An example is the dissociation of HCN:

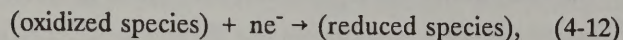
	$\Delta_r G^\circ, \text{ kJ}$	$\log K$	$K$
$\text{HCN} \rightarrow \text{H}^+ + \text{CN}^-$	+52.6	-9.21	$6.2 \times 10^{-10}$
$\text{CN}^- + \text{H}^+ \rightarrow \text{HCN}$	-52.6	+9.21	$1.6 \times 10^9$

For two or more reactions in sequence, the standard Gibbs energy changes  $\Delta_r G^\circ$  and the  $\log K$  values are added, and the  $K$  values are multiplied to give the values for the combined reactions. For example:

	$\Delta_r G^\circ, \text{ kJ}$	$\log K$	$K$
$\text{CN}^- + \text{H}^+ \rightarrow \text{HCN}$	-52.6	+9.21	$1.6 \times 10^9$
$\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$	+79.9	-14.00	$1.0 \times 10^{-14}$
$\text{CN}^- + \text{H}_2\text{O} \rightarrow \text{HCN} + \text{OH}^-$	+27.3	-4.79	$1.6 \times 10^{-5}$

### Redox Reactions

Redox half-reactions are by convention written as reductions:



where  $\text{e}^-$  = electron

and  $n$  = number of electrons.

The standard reduction potential  $E^\circ$  of half-reaction 4-12 is given by

$$E^\circ = -\Delta_{\text{hr}} G^\circ / nF, \quad (4-13)$$

where  $\Delta_{\text{hr}} G^\circ$  = standard Gibbs energy change for the half-reaction,

$n$  = number of electrons transferred,

and  $F$  = Faraday constant,  $96.485 \text{ kJ} \cdot \text{V}^{-1} \cdot \text{equiv}^{-1}$ .

The potential  $E$  of a half-reaction in any solution is related to the standard potential  $E^\circ$  by the Nernst equation:

$$E = E^\circ - (RT/nF) \ln Q \quad (4-14)$$

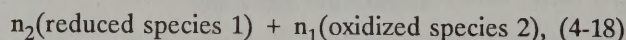
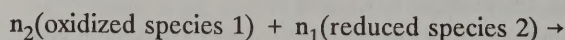
$$= E^\circ - (2.3026RT/nF) \log Q \quad (4-15)$$

$$= E^\circ - 0.05916 \log Q \text{ at } 25^\circ \text{ C}, \quad (4-16)$$

$$\text{where } \log Q = \log a_{\text{Ox}} - \log a_{\text{Rd}}, \quad (4-17)$$

where  $a_{\text{Ox}}$  and  $a_{\text{Rd}}$  = activities of the oxidized and reduced species, respectively.

For the redox reaction



the thermodynamic quantities are

$$E_r^\circ = E_1^\circ - E_2^\circ, \quad (4-19)$$

$$\Delta_r G^\circ = -n_1 n_2 F E_r^\circ, \quad (4-20)$$

and, from equations 4-8 and 4-9,

$$\log K = n_1 n_2 F E_r^\circ / 2.3026 RT \quad (4-21)$$

$$= 5039.7 n_1 n_2 E_r^\circ / T \quad (4-22)$$

$$= n_1 n_2 E_r^\circ / 0.05916 \text{ at } 25^\circ \text{ C}. \quad (4-23)$$

### Activity, Activity Coefficients, and Equilibrium Constants

The definition of the thermodynamic equilibrium constant  $K$  was given above in equations 4-10 and 4-11 in terms of activities rather than concentrations. In this section, activity and activity coefficient are defined, and the relationship of experimentally determined equilibrium constants to the thermodynamic equilibrium constant is described.



The activity of a pure solid or liquid species is equal to 1 by definition. For a dissolved species, the activity  $a$  is related to the concentration  $c$  by the dimensionless activity coefficient  $\gamma$ :

$$a = \gamma c. \quad (4-24)$$

For aqueous solutions,  $\gamma$  approaches 1 as  $c$  approaches zero, so that at very low concentrations,  $a = c$ . For aqueous species the standard state is defined as unit activity, which is equivalent to a hypothetical ideal concentration of 1 mol solute per kilogram  $H_2O$  with  $\gamma = 1$ .

As noted, the thermodynamic equilibrium constant  $K$  for a reaction is defined in terms of activities rather than concentrations. However, equilibrium constants are usually determined experimentally in terms of concentrations. Equilibrium constants thus determined are called concentration equilibrium constants  $K_c$ . According to equation 4-24, activity coefficients vary with concentration, so concentration equilibrium constants must be determined under conditions where activity coefficients are constant. This is achievable by conducting the determinations in solutions that contain an added inert electrolyte. The concentrations of the species that participate in the equilibrium being studied are usually maintained at low values relative to the concentration of added inert electrolyte. Under these conditions, all activity coefficients depend only on the concentration of inert electrolyte. The variation of the activity coefficients with inert electrolyte concentration is proportional to the sum of the concentrations and squared charges of the ions, a quantity termed the "ionic strength." The ionic strength is defined and discussed in appendix A. When equilibrium constants are reported, the ionic strength must therefore be specified, along with the temperature. To obtain the thermodynamic equilibrium constant  $K$ , the concentration equilibrium constant  $K_c$  is determined at several different values of ionic strength. A plot of  $\log K_c$  versus ionic strength approaches  $\log K$  as the ionic strength approaches zero, and  $\log K$  is accordingly obtained by extrapolation. In practice,  $K_c$  may be approximated as  $K$  at ionic strengths below 0.01M.

The notation in use for equilibrium constants requires comment. In the literature on equilibrium data, the symbol  $K$  is usually used for equilibrium constants both at zero and finite ionic strengths. In multistep equilibria such as metal complex formation, the symbol  $K$  is usually used for single-step equilibria (e.g.,  $ML_2 + L \leftrightarrow ML_3$ , with metal ion  $M$  and ligand  $L$ ) and  $\beta$  for cumulative equilibria (e.g.,  $M + 3L \leftrightarrow ML_3$ ). Martell and Smith (1-4)<sup>1</sup> in their authoritative compilations use only the symbol  $K$ , and that

practice will be followed in this publication. Appropriate subscripts will be used where necessary to distinguish  $K$  values for different equilibria, as in the examples discussed in the last section of this chapter.

## DATA AND SOURCES

This section outlines the data requirements and data sources pertinent to aqueous chemical equilibria of interest in cyanide systems. The data tables in this publication are described.

### Data Requirements

Thermodynamic data are required for delineating the chemical equilibria in any system. In the context of this publication, data are required for the following categories of chemical species:

- Free cyanide and derived species.
- Solid and dissolved metal cyanide species.
- Auxiliary species.
- Metal oxides, hydroxides, and aqueous ions.
- Species that may react with cyanide and derived species.
- Species that may precipitate or complex with metal ions.
- Solid metal compounds and soluble metal complexes with auxiliary species.

For equilibria at 25° C, the required data consist of the standard Gibbs energies of formation  $\Delta_f G^\circ$  of each chemical species. The standard enthalpies of formation  $\Delta_f H^\circ$  and entropies  $S^\circ$  of the chemical species are required for equilibria at other temperatures.

Chemical equilibria depend on other variables that are readily measured:

- Temperature.
- Pressure.
- pH.
- Oxidation-reduction (redox) potential.
- Ionic strength.

The pH is measurable by means of a glass electrode and is not the same as acidity or alkalinity determined by titration.

The redox potential may be measured relative to any reference electrode, then converted to the value relative to the standard  $H^+/H_2$  electrode. Redox potentials in thermodynamic or equilibrium data compilations are always relative to the standard  $H^+/H_2$  electrode.

The concept of ionic strength is reviewed in appendix A. A conductivity measurement may be used to estimate

<sup>1</sup>Italic numbers in parentheses refer to items in the list of references at the end of this chapter.



the ionic strength if most of the total electrolyte concentration is due to a single salt, e.g., NaCl. In such cases, the salt concentration may be determined from conductivity versus concentration data. Otherwise, chemical analysis of the solution is required.

### Summary of Data Tables

The thermodynamic data are compiled in appendixes B, C, and D. An outline of the tabulated data and the major source compilations follows:

Table B-1:  $\Delta_f H^\circ$  and  $\Delta_f G^\circ$  for free cyanide and derived species at 25° C. The major source is the NBS tables (5).

Table B-2: Log K for aqueous reactions of free cyanide and derived species. Data are tabulated for temperatures 0°, 10°, 25°, 40°, 60°, and 90° C and ionic strengths 0M, 0.1M, 1.0M, and 3.0M. The temperature range includes temperatures for published reaction rate data as well as temperatures likely to be encountered in practice. The major data sources are the compilations of Martell and Smith (1-4) and Christensen and others (6).

Table B-3: Solubilities of compounds derived from or related to cyanide. These data were used to obtain some of the values in table B-1, as shown by the references cited.

Table C-1:  $\Delta_f H^\circ$  and  $\Delta_f G^\circ$  for auxiliary species at 25° C. The format is the same as in table B-1. The major data sources are the NBS tables (5) and a CODATA report (7).

Table C-2: Log K for aqueous reactions of auxiliary species. The format is the same as in table B-2. The major data sources are the compilations of Martell and Smith (1-4) and Christensen and others (6). The review of Wilhelm and others (8) provided sources of gas solubility data.

Table D-1:  $\Delta_f G^\circ$  for aqueous metal ions at 25° C. The NBS tables (5) and the CODATA report (7) provided some data; more recent primary sources (listed in appendix D) also provided many values.

Tables D-2 through D-24: Log K for formation of solid metal compounds and soluble metal complexes in aqueous solution at 25° C and ionic strength 0, 0.1, 1.0, and 3.0M. Data for equilibria at other temperatures are insufficient for doing meaningful calculations, so they are not given here. Tables D-2 through D-23 also include  $\Delta_f G^\circ$  values for solid metal compounds and metal species in aqueous solution at 25° C. Most of the equilibrium data are from Martell and Smith (1-4). Additional equilibrium data for metal ion hydrolysis and precipitation of hydrous metal oxides were obtained from Baes and Mesmer (9). Gibbs energies of formation of metal oxides and sulfides were taken mainly from USBM bulletins (10-11); the compilation of Mills (12) was also consulted for metal sulfides.

Data for metal cyanide species were also obtained from the monograph by Sharpe (13) and the review by Beck (14).

For all of the tables in appendixes B, C, and D, primary sources were consulted for more extensive or more recent data. These primary sources are referenced in the respective appendixes and cited in the columns "Additional references."

### Additional Details Concerning Data for Metal Species

Older references for thermodynamic data on metal species, such as Latimer (15), Garrels and Christ (16), Sillen and Martell (17-18), or Pourbaix (19) are obsolete. The recent compilation of Bard and others (20) is a successor to Latimer (15). In its attempt to be comprehensive, it references some of the older compilations (15, 17-19, 21) for data not located in more recent sources.

The literature contains discrepancies for log K values. Some recent publications on cyanide chemistry in precious-metal hydrometallurgy give tables of log K data for metal cyanide species, some of which are obsolete and unreliable. For example, Huiatt and others (22) and Smith and Mudder (23) compiled values from Sharpe (13); Smith and Mudder (23) also tabulated some data from Caruso (24). Some data quoted by Caruso (24) and Broderius (25) disagree with the compilations of Martell and Smith (1-4). The authors have chosen the most up-to-date and accurate log K data for this report.

Data have been compiled for the aqueous ions and solid compounds and soluble complexes of Zn(II), Cd(II), Hg(I), Hg(II), Cu(I), Cu(II), Ag(I), Au(I), Au(III), Ni(II), Co(II), Co(III), Fe(II), Fe(III), Mn(II), Mn(III), Cr(III), Tl(I), Tl(III), and Pb(II). Species involving Cr(II), V(II), V(III), V(IV), and V(V) are excluded because sufficient thermodynamic data are not available to construct equilibrium predominance area diagrams. No thermodynamic data are available for any vanadium cyanide complexes. Further, V(II), V(III), and Cr(II) are so readily oxidized that they are unlikely to be encountered in hydrometallurgical or environmental situations.

Besides the solid cyanides and soluble cyanide species, data are included for the solid oxides, hydroxides, sulfides, and carbonates, and for the soluble complexes with OH<sup>-</sup>, Cl<sup>-</sup>, SH<sup>-</sup>, S<sub>2</sub>O<sub>3</sub><sup>2-</sup> (thiosulfate), SO<sub>4</sub><sup>2-</sup> (sulfate), NCS<sup>-</sup> (thiocyanate), and NH<sub>3</sub> (ammonia). Data are also included for the aqueous ions, hydroxides, and carbonate and sulfate species of magnesium and calcium.

In the thermodynamics tables, coordinated H<sub>2</sub>O is omitted from all species, including complexes often formulated with coordinated H<sub>2</sub>O such as amine and cyanide complexes of Co, Cr, or Fe. For example, [Fe(CN)<sub>5</sub>(H<sub>2</sub>O)]<sup>3-</sup> is tabulated as [Fe(CN)<sub>5</sub>]<sup>3-</sup>.



The log K values for reactions of metal species are rounded to the nearest 0.1 unit, because the accuracy of most experimental determinations is of that order of magnitude. An uncertainty of 0.10 in log K° at 25° C corresponds to an uncertainty of 0.57 kJ in  $\Delta_f G^\circ$ , in accordance with equation 4-8. The  $\Delta_f G^\circ$  values for metal oxides and sulfides taken from the literature are rounded to the nearest 1 kJ·mol<sup>-1</sup>, which corresponds to the accuracy of most of the data.

Often data are not given for zero ionic strength. Estimated values at zero ionic strength were made by comparison with analogous systems for which data at zero and finite ionic strengths are available (1-4). Details of these estimates are given with the data in tables D-2 through D-23.

For metal oxides and sulfides, the  $\Delta_f G^\circ$  values were combined with  $\Delta_f G^\circ$  data for the metal ions (table D-1) and H<sub>2</sub>O, OH<sup>-</sup>, or H<sub>2</sub>S (table C-1) to calculate log K

values for solubility equilibria at zero ionic strength. For all other species, the log K values at zero ionic strength were combined with  $\Delta_f G^\circ$  values for metal ions (table D-1), cyanide and derived species (table B-1), and auxiliary species (table C-1), to calculate  $\Delta_f G^\circ$  values via equation 4-8. Values of  $\Delta_f G^\circ$  in tables D-2 through D-23 thus obtained from log K values are calculated to 0.1·kJ·mol<sup>-1</sup> precision to minimize roundoff errors during subsequent calculations.

Generally, any given metal ion does not form complexes or insoluble compounds with all of the auxiliary species mentioned above. A summary of the existence of metal complexes and insoluble compounds is given in table 4-1. Table 4-1 also indicates the accuracy of the published log K data for metal species and the generation of estimates where data are not available. Full details are given in tables D-2 through D-23.

Table 4-1.-Existence of metal complexes<sup>1</sup> and basis of thermodynamic data<sup>2</sup>

Metal ion	M <sup>n+</sup> (aq)	CN <sup>-</sup>		O <sup>2-</sup> , OH <sup>-</sup>	OH <sup>-</sup>	Cl <sup>-</sup>		S <sup>2-</sup>	SH <sup>-</sup>	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	SO <sub>4</sub> <sup>2-</sup>		NH <sub>3</sub>	CO <sub>3</sub> <sup>2-</sup>	NCS <sup>-</sup>	
		c	s			c	s				c	s			c	s
Zn(II)	A	A	R	A	R	R		R	I	I	I		A	U	R	
Cd(II)	A	A	U	A	U	R		R	I	I	I		A	U	R	
Hg(I)	A	N	N	N	R	N	A	N	N	N	I	A	N	U	N	A
Hg(II)	A	A	A	A	R	I	R	R	I	I	I		I	U	R	R
Cu(I)	A	U	U	A	X	I	R	R	X	I	X		I	N	I	U
Cu(II)	A	O		A	R	R		R	O	O	R		A	U	R	
Ag(I)	A	A	A	A	A	R	A	A	U	I	R		A	R	R	R
Au(I)	U	E	E	X	E	E	U	U	U	E	X		E	N	E	X
Au(III)	U	E		R	E	E		O	O	O	W		E	N	EX	
Ni(II)	A	A	R	A	U	I		R	N	N	R		A	U	I	
Co(II)	A	U	X	A	U	I		R	N	N	R		R	U	I	
Co(III)	R	E		UX	X	XO		O	O	O	X		E	N	O	
Fe(II)	A	R	X	A	U	X		R	N	N	X		X	U	U	
Fe(III)	A	R		A	R	R		O	O	O	R		N	N	R	
Mn(II)	R	E	X	A	UX	I		R	O	O	R		I	U	I	
Mn(III)	R	E		A	IX	XO		O	O	O	X		N	N	O	
Cr(III)	U	E		RU	I	IX		U	N	N	X		E	N	IX	
Tl(I)	A	N		N	N	R	A	R	I	I	R		N	N	I	R
Tl(III)	R	I		R	R	R		O	O	O	IX		N	N	O	
Pb(II)	A	N		A	R	R	R	R	N	I	R	R	N	U	I	R

<sup>1</sup>aq, aqueous; c, in solution; s, solid phase.

<sup>2</sup>More than one symbol may be entered if several species exist:

A Reliable published data,  $\pm 1$  kJ·mol<sup>-1</sup> or better.

E Estimates based on incomplete data.

I Data at finite ionic strengths; data at zero ionic strength estimated.

N No data; complexes probably weak or species not likely to exist under anticipated conditions.

O Redox reaction.

R Reliable published data,  $\pm 1-3$  kJ·mol<sup>-1</sup>.

U Published data of uncertain accuracy,  $\pm 3$  or more kJ·mol<sup>-1</sup>.

X No published data; estimates based on qualitative information or trends in data for related systems.



## EQUILIBRIUM PREDOMINANCE AREA DIAGRAMS

Equilibrium data are presented in appendix E in the form of equilibrium predominance area diagrams (EPAD, singular or plural). An EPAD shows the predominant chemical species in a system as a function of certain independent variables. The independent variables are chosen based on the nature of the system and the information to be displayed.

This section discusses the variables involved in EPAD for aqueous equilibria; the treatment of solution, solid, and gaseous species; the construction of EPAD; and the reliability of EPAD.

### Variables in EPAD for Aqueous Systems

For aqueous systems, an EPAD shows the predominant chemical species in a system as a function of temperature, pressure, and composition variables. Temperature and total pressure are constant in all EPAD in this publication at values of 25° C (298.15 K or 77° F) and 10<sup>5</sup> Pa (1 bar or (1/1.01325) atm), respectively. The four composition variables are pH, pM, pL, and Eh:

- $\text{pH} = -\log(\text{activity of } \text{H}^+) = -\log a(\text{H}^+)$ .
- $\text{pM} = -\log(\text{total activity of all dissolved metal species})$ . For example, if M is zinc,  $\text{pM} = \text{pZn} = -\log [a(\text{Zn}^{2+}) + a(\text{Zn}(\text{OH})^+) + a(\text{Zn}(\text{OH})_2) + \dots + \text{terms for each of all other dissolved Zn species}]$ . This total includes complexes, e.g., the  $\text{Zn}^{2+}/\text{CN}^-$  species if  $\text{HCN}/\text{CN}^-$  is present as a ligand. If more than one metal is present, separate pM's are defined for each metal. For example, if zinc and copper are both present,  $\text{pM}' = \text{pZn}$  and  $\text{pM}'' = \text{pCu}$  are used.
- $\text{pL} = -\log(\text{total activity of free ligand species})$ . For example, if L is cyanide,  $\text{pL} = \text{pCN} = -\log [a(\text{CN}^-) + a(\text{HCN})]$ ; if L is carbonate,  $\text{pL} = \text{pCO}_3 = -\log [a(\text{CO}_3^{2-}) + a(\text{HCO}_3^-) + a(\text{CO}_2(\text{aq}))]$ . If more than one ligand is present, separate pL's are defined for each ligand. For example, if cyanide and carbonate are both present,  $\text{pL}' = \text{pCN}$  and  $\text{pL}'' = \text{pCO}_3$  are used.
- Eh = reduction potential relative to the standard  $\text{H}^+/\text{H}_2$  electrode,  $\text{E}^\circ[2\text{H}^+ + 2\text{e}^- = \text{H}_2(\text{g})] = 0$ .

To generate EPAD, two of these four composition variables are chosen as independent variables, and the other two are held constant. The six possible kinds of EPAD, therefore, include the following:

- Eh-pH diagrams (pM, pL constant).
- pM-pH diagrams (Eh, pL constant).
- pM-pL diagrams (Eh, pH constant).
- pL-pH diagrams (Eh, pM constant).
- Eh-pM diagrams (pH, pL constant).
- Eh-pL diagrams (pM, pH constant).

Not all four composition variables may be involved in an EPAD. For example, a pL-pH diagram may be drawn to show the equilibria of a ligand without any metal ions. Constant oxidation state is often used as an alternative to constant Eh. The choice among these six kinds of EPAD depends on the problem of interest, as shown by examples in chapter 11.

### Solution Species

EPAD are constructed from thermodynamic data, which consist of  $\Delta_f G^\circ$  data for all of the species in the system. Hence, they are based on activities of species, which become numerically equal to concentrations at ionic strengths below 0.1M. Because they are based on activities, EPAD are independent of ionic strength. At ionic strengths above 0.1M, equation 4-24 may be used with known or estimated activity coefficients to obtain concentrations.

### Solid Phases

If slightly soluble solid phases, e.g., metal compounds, exist, EPAD can be constructed to show the approximate solubility contours. The solubility contours are approximate; they give solubilities lower than the true values to the extent that the predominant solution species in equilibrium with the solid phase constitutes less than 100 pct of the total solution species in equilibrium with that solid phase.

### Gaseous Species

If a gaseous species, e.g., a volatile free-ligand species, is involved, approximate isobars for its partial pressure in the system can be displayed on EPAD. The isobars are approximate to the extent that the predominant solution species in equilibrium with the gaseous species constitutes less than 100 pct of the total solution species in equilibrium with that gaseous species.

### Construction of EPAD

EPAD are constructed via computer programs, typically by the following procedure:

1. Inputting the standard Gibbs energies of formation  $\Delta_f G^\circ$  of all species;
2. Writing all possible reactions between species;
3. Calculating the standard Gibbs energy changes  $\Delta_r G^\circ$  and equilibrium constants K of each of the reactions according to equations 4-4 and 4-8;
4. Expressing the equilibria for the reactions as equations in logarithmic form in accordance with equation 4-11;



5. Plotting these equations against the chosen independent composition variables;

6. Examining the plots to determine the predominant species, and retaining only those equations and plots that define the areas of predominant species. Each predominant species occupies an area bounded by straight lines, which separate it from areas occupied by other predominant species. The straight lines that bound the areas of predominant species correspond to the equilibria that relate them.

For this publication, EPAD were generated by the program "SYSTEM," which is part of the CSIRO-SGTE thermodynamics program package (26). The input to the SYSTEM program consists of the standard Gibbs energies  $\Delta_f G^\circ$  of formation of all species (tables B-1, C-1, and D-1 through D-23), along with the other parameters required to specify the desired diagram.

### Reliability of EPAD

To obtain reliable diagrams, reliable thermodynamic data must be input. Unfortunately, some of the compilations often cited by authors of published diagrams are obsolete. In this report, much effort was made to obtain the most reliable thermodynamic data. A large number of EPAD were calculated from the thermodynamic data in tables B-1, C-1, and D-1 through D-23 and are presented in appendix E.

Osseo-Asare and others (27) published EPAD for metal-cyanide systems in 1984. The data base from which their diagrams are generated is not completely up to date; the references cited there include some of the obsolete references mentioned previously (15-17, 19). Consequently, the accuracy of their diagrams is limited. In the case of cobalt, the diagram is incorrect because of erroneous information on the cyanide complexes.

Wang and Forssberg (28) published several EPAD in 1990, involving metal cyanide species. They cited Smith and Martell (1), Bard and others (20), and some of the older compilations (16-18) for their input data. Overall, their input data are more recent and more reliable than the data used by Osseo-Asare and others (27).

In systems where there are known species for which no thermodynamic data are available, those species are usually not shown in published EPAD (27-28). This can result in misleading diagrams. If sufficient data are not available, estimates of the missing data should be employed and specified. Tolerable estimates can be made from semiquantitative or even qualitative chemical information about the system. Otherwise, the EPAD should be clearly labeled or captioned with regard to missing data. In this publication, missing data were estimated; the details

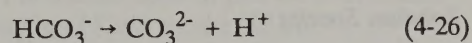
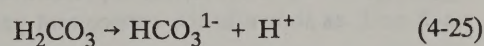
of the estimates are given in the data tables in appendixes B, C, and D.

### INFORMATION OBTAINABLE BY INSPECTION OF LOG K DATA

A list of equilibria and log K values for a system may seem bewildering. However, it is possible, as shown below, to extract useful information from log K data tables and visualize what EPAD for a system look like. All of the data in the examples below are taken from the tables in appendixes C and D. The following examples include a polyprotic acid, metal ion hydrolysis, and some systems of metal complexes.

#### Example 1: Polyprotic Acid

For an example of a polyprotic acid, consider the pL-pH EPAD for carbonic acid ( $\text{H}_2\text{CO}_3$ ). The equilibria are as follows:



$$K_{a1} = [\text{HCO}_3^-][\text{H}^+]/[\text{H}_2\text{CO}_3] = 1/K_{f2} \quad (4-27)$$

$$K_{a2} = [\text{CO}_3^{2-}][\text{H}^+]/[\text{HCO}_3^-] = 1/K_{f1} \quad (4-28)$$

For acid dissociation equilibria, the notation  $\text{p}K_a = -\log K_a$  is commonly used. The  $\log K_f$  notation is introduced to show the similarity of polyprotic acid dissociation equilibria with metal-ligand equilibria described subsequently. Multiplication of equation 4-27 by equation 4-28 gives

$$\begin{aligned} K_{a12} &= [\text{CO}_3^{2-}][\text{H}^+]^2/[\text{H}_2\text{CO}_3] = 1/K_{f12} \\ &= K_{a1}K_{a2} = 1/K_{f2}K_{f1}. \end{aligned} \quad (4-29)$$

The values are  $\log K_{a1} = -\text{p}K_{a1} = -\log K_{f2} = -6.3$  and  $\log K_{a2} = \text{p}K_{a2} = -\log K_{f1} = -10.3$ , from table C-2. From equation 4-29,  $K_{a12} = 1/K_{f12} = 10^{-16.6}$ , or  $\log K_{a12} = -\log K_{f12} = -16.6$ . The quantities  $K_{f1}$ ,  $K_{f2}$ , and  $K_{f12}$  constitute formation constants of  $\text{HCO}_3^-$  and  $\text{H}_2\text{CO}_3$  from  $\text{CO}_3^{2-}$  and  $\text{H}^+$ .  $K_{f1}$  and  $K_{f2}$  are stepwise formation constants, and  $K_{f12}$  is the cumulative formation constant. This formation constant terminology exactly parallels the terminology for metal complexes as shown below. From the data, equations 4-27 and 4-28, and the definition of predominance areas, the values

$$\begin{aligned} \text{pH}_{12} &= 6.3 = -\log [\text{H}^+]_{12} \\ &= -\log K_{a1} = \log K_{f2} \end{aligned} \quad (4-30)$$



$$\begin{aligned} \text{and} \quad \text{pH}_{01} &= 10.3 = -\log [\text{H}^+]_{01} \\ &= -\log K_{a2} = \log K_{f1} \end{aligned} \quad (4-31)$$

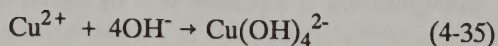
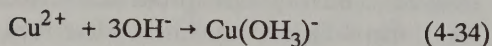
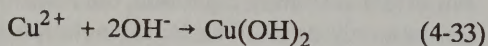
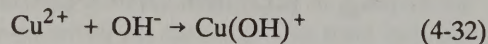
divide the predominance areas  $\text{H}_2\text{CO}_3$  versus  $\text{HCO}_3^-$  and  $\text{HCO}_3^-$  versus  $\text{CO}_3^{2-}$ , respectively. Thus in a pL-pH EPAD of a weak acid, the boundaries of the predominance areas occur at pH values equal to the  $\text{pK}_a = -\log K_a$  values. The  $\text{H}_2\text{CO}_3$  example is illustrated in figure E-2.

### Example 2: Hydrolyzable Metal Ion

The hydrolysis of metal ions results from the fact that metal ions behave like polyprotic acids. Alternatively, the hydrolysis of metal ions can be viewed as complex formation of the metal ions with the ligand  $\text{OH}^-$ . Metal ion hydrolysis equilibria are tabulated by Martell and Smith (1-4) and in appendix D in terms of the cumulative formation constants from the metal ion and  $\text{OH}^-$ . These equilibria can be alternatively expressed as ionization of a weak acid, as shown in the subsequent paragraph.

#### Solution Species

As an example, consider the hydrolysis of  $\text{Cu}^{2+}$  and the corresponding pM-pH EPAD. The equilibria are



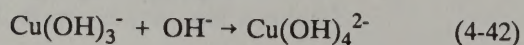
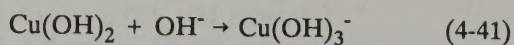
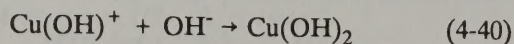
$$K_{f1} = [\text{Cu}(\text{OH})^+]/[\text{Cu}^{2+}][\text{OH}^-] \quad (4-36)$$

$$K_{f12} = [\text{Cu}(\text{OH})_2]/[\text{Cu}^{2+}][\text{OH}^-]^2 \quad (4-37)$$

$$K_{f123} = [\text{Cu}(\text{OH})_3^-]/[\text{Cu}^{2+}][\text{OH}^-]^3 \quad (4-38)$$

$$K_{f1234} = [\text{Cu}(\text{OH})_4^{2-}]/[\text{Cu}^{2+}][\text{OH}^-]^4 \quad (4-39)$$

Note the similarity of equations 4-36 through 4-39 to equations 4-27 and 4-28. The tabulated values are  $\log K_{f1} = 6.5$ ,  $\log K_{f12} = 11.8$ ,  $\log K_{f123} = 15.0$ , and  $\log K_{f1234} = 16.4$ , from table D-7. To visualize the equilibria, the remaining stepwise equilibria are derived:



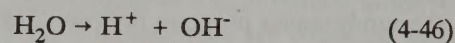
$$K_{f2} = [\text{Cu}(\text{OH})_2]/[\text{Cu}(\text{OH})^+][\text{OH}^-] \quad (4-43)$$

$$K_{f3} = [\text{Cu}(\text{OH})_3^-]/[\text{Cu}(\text{OH})_2][\text{OH}^-] \quad (4-44)$$

$$K_{f4} = [\text{Cu}(\text{OH})_4^{2-}]/[\text{Cu}(\text{OH})_3^-][\text{OH}^-] \quad (4-45)$$

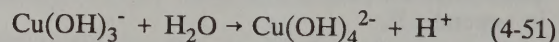
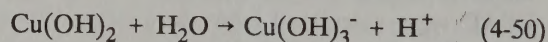
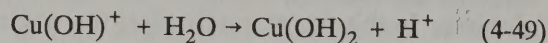
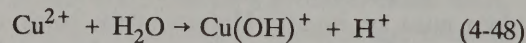
The second stepwise constant,  $\log K_{f2}$ , is defined by equations 4-40 and 4-43, and is  $11.8 - 6.5 = 5.3$ . Similarly,  $\log K_{f3}$  from equations 4-41 and 4-44 is 3.2, and  $\log K_{f4}$  from equations 4-42 and 4-45 is 1.4.

To obtain pH values for visualizing the EPAD, the equilibrium for the dissociation of  $\text{H}_2\text{O}$ ,



$$K_w = [\text{H}^+][\text{OH}^-], \quad (4-47)$$

with  $\log K_w = -\text{p}K_w = -14.0$ , is required. By combining equations 4-46 and 4-47 with the stepwise equilibria 4-32, 4-36, and 4-40 through 4-45, the equilibria are expressed as acid dissociations:



$$K_{a1} = [\text{Cu}(\text{OH})^+][\text{H}^+]/[\text{Cu}^{2+}] \quad (4-52)$$

$$K_{a2} = [\text{Cu}(\text{OH})_2][\text{H}^+]/[\text{Cu}(\text{OH})^+] \quad (4-53)$$

$$K_{a3} = [\text{Cu}(\text{OH})_3^-][\text{H}^+]/[\text{Cu}(\text{OH})_2] \quad (4-54)$$

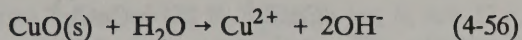
$$K_{a4} = [\text{Cu}(\text{OH})_4^{2-}][\text{H}^+]/[\text{Cu}(\text{OH})_3^-] \quad (4-55)$$

Therefore  $\log K_{a1} = 6.5 - 14.0 = -7.5$ , and similarly,  $\log K_{a2} = -8.7$ ,  $\log K_{a3} = -10.8$ , and  $\log K_{a4} = -12.6$ . The pH values 7.5, 8.7, 10.8, and 12.6 divide the respective predominance areas of  $\text{Cu}^{2+}$ ,  $\text{Cu}(\text{OH})^+$ ,  $\text{Cu}(\text{OH})_2$ ,  $\text{Cu}(\text{OH})_3^-$ , and  $\text{Cu}(\text{OH})_4^{2-}$ . Thus, in a pM-pH EPAD of the hydrolysis of a metal ion, the boundaries of the predominance areas occur at pH values equal to the  $\text{pK}_a = -\log K_a$  values for the metal ion considered as a polyprotic acid.

#### Slightly Soluble Compounds

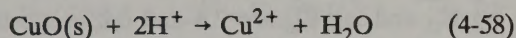
Slightly soluble metal oxide compounds universally appear in the hydrolysis of metal ions. In this example, they are amorphous or crystalline  $\text{Cu}(\text{OH})_2$  or  $\text{CuO}$ . To illustrate with  $\text{CuO}$ ,





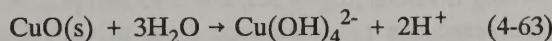
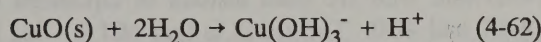
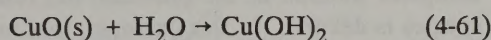
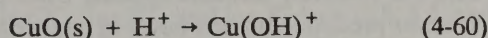
$$K_{s0} = [\text{Cu}^{2+}][\text{OH}^-]^2. \quad (4-57)$$

The value of  $\log K_{s0}$  is -20.4. Expressing this equilibrium in terms of  $\text{H}^+$ , equations 4-56 and 4-57 with the aid of equations 4-46 and 4-47 are replaced by



$$K_{s0}^* = [\text{Cu}^{2+}]/[\text{H}^+]^2. \quad (4-59)$$

The value of  $\log K_{s0}^*$  is  $-20.4 + 28.0 = 7.6$ . Next, the equilibria of  $\text{CuO(s)}$  with the hydrolyzed species are written with the aid of equations 4-48 through 4-55:



$$K_{s1}^* = [\text{Cu(OH)}^+]/[\text{H}^+] \quad (4-64)$$

$$K_{s2}^* = [\text{Cu(OH)}_2] \quad (4-65)$$

$$K_{s3}^* = [\text{Cu(OH)}_3^-][\text{H}^+] \quad (4-66)$$

$$K_{s4}^* = [\text{Cu(OH)}_4^{2-}][\text{H}^+]^2 \quad (4-67)$$

The respective values of  $\log K_{s1}^*$  through  $K_{s4}^*$  are 0.1, -8.6, -19.4, and -32.0. By combining this information with the hydrolysis species predominance areas obtained in the preceding paragraph, and equations 4-64 through 4-67, the solubility curve for  $\text{CuO(s)}$  is obtained. The curve is divided into segments that correspond to the pH region of predominance of each solution species. The  $\text{CuO(s)}$  solubility curve runs from  $\text{pM} = 0$  at  $\text{pH} = 3.8$ , to  $\text{pM} = 7.4$  at  $\text{pH} = 7.5$ , to  $\text{pM} = 8.6$  at  $\text{pH} = 8.7$ , to  $\text{pM} = 8.6$  at  $\text{pH} = 10.8$ , to  $\text{pM} = 6.8$  at  $\text{pH} = 12.6$ , to  $\text{pM} = 4.0$  at  $\text{pH} = 14.0$ . The EPAD for  $\text{Cu}_{2+}$  hydrolysis with  $\text{CuO(s)}$  is illustrated in figure E-95.

As indicated above, the solid phase may be some oxide other than  $\text{CuO}$ . Consider the case where the solid phase is amorphous  $\text{Cu(OH)}_2$ . The values of  $\log K_{s0}$  and  $\log K_{s0}^*$  for the equilibria corresponding to equations 4-56 through 4-59 are respectively -18.8 and 9.2. These values are 1.6 units more positive than the values for  $\text{CuO(s)}$ , so amorphous  $\text{Cu(OH)}_2$  is more soluble. Per mole of  $\text{H}^+$ , the values are 0.8 units higher. The result is that on the EPAD, the solubility curve for amorphous  $\text{Cu(OH)}_2$  is shifted -0.8 pM units relative to the curve for  $\text{CuO(s)}$ .

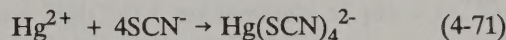
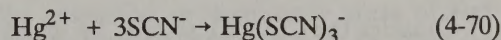
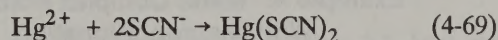
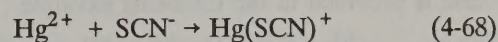
Although this example appears long and time consuming, it is straightforward, and one can perform the computations easily in tabular form. To summarize, the computation may be diagramed, where  $n$  = number of  $\text{OH}^-$  groups bound to  $\text{Cu}^{2+}$ . The arrows indicate the path through which the computations are executed:

$n$	$\log K_{f1..n}$	$\log K_n$	$\log K_{an}$	$\log K_{sn}^*$	$\text{pM, pH}$
0	—	—	—	7.6 →	0.0, 3.8 ↓
1	6.5 → ↓	6.5 →	-7.5 →	0.1 → ↓	7.4, 7.5 ↓
2	11.8 → ↓	5.3 →	-8.7 →	-8.6 → ↓	8.6, 8.7 ↓
3	15.0 → ↓	3.2 →	-10.8 →	-19.4 → ↓	8.6, 10.8 ↓
4	16.4 →	1.4 →	-12.6 →	-32.0 →	6.8, 12.6 ↓ 4.0, 14.0

The values pM, pH in the last column give the coordinates of the solubility profile of  $\text{CuO}$  on the EPAD.

### Example 3: Metal Complex Formation

The dissociation equilibria of polyprotic acids and the formation equilibria of metal complexes are mathematically analogous, as demonstrated below. For the first example of metal complexes, consider the  $\text{Hg}^{2+}$  -  $\text{SCN}^-$  system. The cumulative formation equilibria are



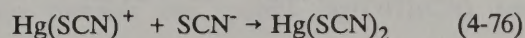
$$K_{f1} = [\text{Hg(SCN)}^+]/[\text{Hg}^{2+}][\text{SCN}^-] \quad (4-72)$$

$$K_{f12} = [\text{Hg(SCN)}_2]/[\text{Hg}^{2+}][\text{SCN}^-]^2 \quad (4-73)$$

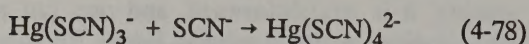
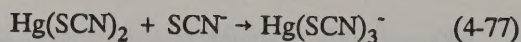
$$K_{f123} = [\text{Hg(SCN)}_3^-]/[\text{Hg}^{2+}][\text{SCN}^-]^3 \quad (4-74)$$

$$K_{f1234} = [\text{Hg(SCN)}_4^{2-}]/[\text{Hg}^{2+}][\text{SCN}^-]^4 \quad (4-75)$$

The respective values of  $\log K_n$  through  $\log K_{f1234}$  are 9.2, 17.3, 20.0, and 21.8, from table D-5. The remaining stepwise equilibria are







$$K_{f2} = [\text{Hg}(\text{SCN})_2]/[\text{Hg}(\text{SCN})^+][\text{SCN}^-] \quad (4-79)$$

$$K_{f3} = [\text{Hg}(\text{SCN})_3^-]/[\text{Hg}(\text{SCN})_2][\text{SCN}^-] \quad (4-80)$$

$$K_{f4} = [\text{Hg}(\text{SCN})_4^{2-}]/[\text{Hg}(\text{SCN})_3^-][\text{SCN}^-] \quad (4-81)$$

The respective values of  $\log K_{f2}$ ,  $\log K_{f3}$ , and  $\log K_{f4}$ , defined by equations 4-76 through 4-81, are  $17.3 - 9.2 = 8.1$ ,  $20.0 - 17.3 = 2.7$ , and  $21.8 - 20.0 = 1.8$ . It follows in the same way as with a polyprotic acid that the  $\text{pSCN} = -\log [\text{SCN}^-] = \text{pL} = -\log [\text{L}]$  values  $\text{pL}_{01} = 9.2$ ,  $\text{pL}_{12} = 8.1$ ,  $\text{pL}_{23} = 2.7$ , and  $\text{pL}_{34} = 1.8$  divide the respective predominance areas of  $\text{Hg}^{2+}$ ,  $\text{Hg}(\text{SCN})^+$ ,  $\text{Hg}(\text{SCN})_2$ ,  $\text{Hg}(\text{SCN})_3^-$ , and  $\text{Hg}(\text{SCN})_4^{2-}$ .

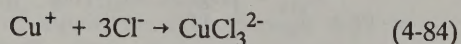
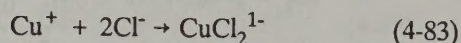
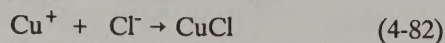
The analogy of metal complex formation and  $\text{pM-pL}$  EPAD versus hydrolyzable metal ions and polyprotic acids and  $\text{pM-pH}$  and  $\text{pL-pH}$  EPAD shows in the correspondence of EPAD variables and the equations above:

$\text{L}^n$ (e.g., $\text{CO}_3^{2-}$ )	$\text{M}^{n+}$ (e.g., $\text{Cu}^{2+}$ )	$\text{M}^{n+}$ (e.g., $\text{Hg}^{2+}$ )
$\text{H}^+$	$\text{H}^+$	$\text{L}$ (e.g., $\text{SCN}^-$ )
$\text{pL-pH}$	$\text{pM-pH}$	$\text{pM-pL}$

In the example of  $\text{Hg}^{2+} - \text{SCN}^-$ , the successive stepwise  $\log K_f$  values are monotonically ordered,  $9.2 > 8.1 > 2.7 > 1.8$ . The significance of this is that every species in the system appears on the EPAD. There are many systems of metal complexes where this is not the case, and such a case is provided in the following example.

#### Example 4: Metal Complex Formation With Disproportionation

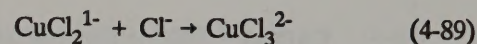
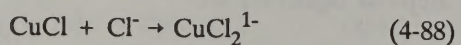
Consider the  $\text{Cu}^+ - \text{Cl}^-$  system, for which the equilibria are



$$K_{f1} = [\text{CuCl}]/[\text{Cu}^+][\text{Cl}^-] \quad (4-85)$$

$$K_{f12} = [\text{CuCl}_2^{1-}]/[\text{Cu}^+][\text{Cl}^-]^2 \quad (4-86)$$

$$K_{f123} = [\text{CuCl}_3^{2-}]/[\text{Cu}^+][\text{Cl}^-]^3 \quad (4-87)$$



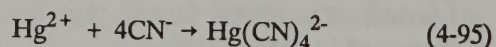
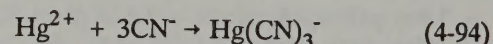
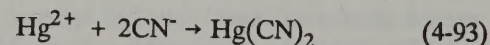
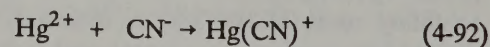
$$K_{f2} = [\text{CuCl}_2^{1-}]/[\text{CuCl}][\text{Cl}^-] \quad (4-90)$$

$$K_{f3} = [\text{CuCl}_3^{2-}]/[\text{CuCl}_2^{1-}][\text{Cl}^-] \quad (4-91)$$

The tabulated data are  $\log K_{f1} = 2.7$ ,  $\log K_{f12} = 5.5$ , and  $\log K_{f123} = 5.7$ , respectively, from table D-6. The values of  $\log K_{f2}$  and  $\log K_{f3}$  are 2.8 and 0.2, respectively. These successive stepwise  $\log K_f$  values are in the order  $2.7 < 2.8 > 0.2$ , so the order is not monotonic. The significance of nonmonotonic ordering of successive stepwise  $\log K_f$  values is that the species responsible for the nonmonotonic ordering is relatively unstable and disproportionates to species with fewer and more bound ligands. The result is that the relatively unstable species,  $\text{CuCl}$  in this example, is never predominant and never appears on an EPAD. To complete solution of the problem, the relatively unstable species is deleted. In this example, that means equations 4-83 and 4-86 are used instead of equations 4-82, 4-85, 4-88, and 4-90. The result is that  $\text{pCl} = -\log [\text{Cl}^-] = \text{pL} = -\log \text{L}$  values  $\text{pL}_{02} = 5.5/2 = 2.75$  and  $\text{pL}_{23} = 0.2$  divide the respective predominance areas of  $\text{Cu}^+$ ,  $\text{CuCl}_2^{1-}$ , and  $\text{CuCl}_3^{2-}$ .

#### Example 5: Metal Complex Formation With a Hydrolyzable Metal Ion and a Ligand Derived From a Weak Acid

When the ligand is derived from a weak acid, or the metal ion hydrolyzes, the picture is complicated by pH dependence of the equilibria. Consider the  $\text{Hg}^{2+} - \text{CN}^-$  system. This system contains both a weak-acid ligand and a hydrolyzable metal ion. The complex-formation equilibria for  $\text{Hg}^{2+}$  and  $\text{CN}^-$  are



$$K_{f1} = [\text{Hg}(\text{CN})^+]/[\text{Hg}^{2+}][\text{CN}^-] \quad (4-96)$$

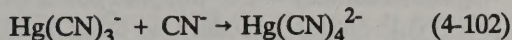
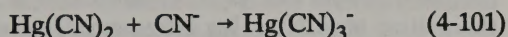
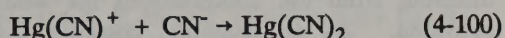
$$K_{f12} = [\text{Hg}(\text{CN})_2]/[\text{Hg}^{2+}][\text{CN}^-]^2 \quad (4-97)$$

$$K_{f123} = [\text{Hg}(\text{CN})_3^-]/[\text{Hg}^{2+}][\text{CN}^-]^3 \quad (4-98)$$

$$K_{f1234} = [\text{Hg}(\text{CN})_4^{2-}]/[\text{Hg}^{2+}][\text{CN}^-]^4 \quad (4-99)$$



The respective values of  $\log K_{f1}$  through  $\log K_{f4}$  are 17.0, 32.8, 36.3, and 39.0, from table D-5. The remaining stepwise equilibria are:

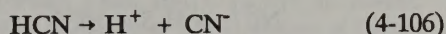


$$K_{f2} = [\text{Hg}(\text{CN})_2]/[\text{Hg}(\text{CN})^+][\text{CN}^-] \quad (4-103)$$

$$K_{f3} = [\text{Hg}(\text{CN})_3^-]/[\text{Hg}(\text{CN})_2][\text{CN}^-] \quad (4-104)$$

$$K_{f4} = [\text{Hg}(\text{CN})_4^{2-}]/[\text{Hg}(\text{CN})_3^-][\text{CN}^-] \quad (4-105)$$

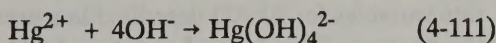
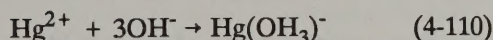
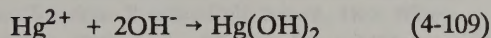
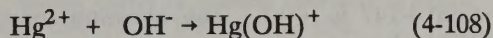
The values of  $\log K_{f2}$ ,  $\log K_{f3}$ , and  $\log K_{f4}$  are 15.8, 3.5, and 2.7, respectively. For the weak acid HCN,



$$K_a = [\text{CN}^-][\text{H}^+]/[\text{HCN}], \quad (4-107)$$

and  $K_a = 9.2$  (table B-2). Consequently, HCN predominates at  $\text{pH} < 9.2$  and  $\text{CN}^-$  at  $\text{pH} > 9.2$ .

For the hydrolysis of  $\text{Hg}^{2+}$ , the equilibria are



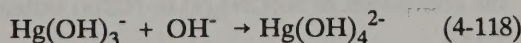
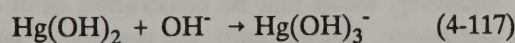
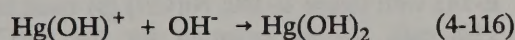
$$K_{f1} = [\text{Hg}(\text{OH})^+]/[\text{Hg}^{2+}][\text{OH}^-] \quad (4-112)$$

$$K_{f12} = [\text{Hg}(\text{OH})_2]/[\text{Hg}^{2+}][\text{OH}^-]^2 \quad (4-113)$$

$$K_{f123} = [\text{Hg}(\text{OH})_3^-]/[\text{Hg}^{2+}][\text{OH}^-]^3 \quad (4-114)$$

$$K_{f1234} = [\text{Hg}(\text{OH})_4^{2-}]/[\text{Hg}^{2+}][\text{OH}^-]^4 \quad (4-115)$$

The tabulated values of  $\log K_{f1}$  through  $\log K_{f1234}$  are 10.6, 21.8, 20.9, and 18.9, respectively, from table D-5. The remaining stepwise equilibria are

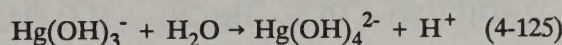
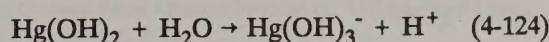
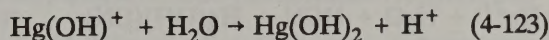
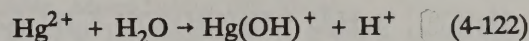


$$K_{f2} = [\text{Hg}(\text{OH})_2]/[\text{Hg}(\text{OH})^+][\text{OH}^-] \quad (4-119)$$

$$K_{f3} = [\text{Hg}(\text{OH})_3^-]/[\text{Hg}(\text{OH})_2][\text{OH}^-] \quad (4-120)$$

$$K_{f4} = [\text{Hg}(\text{OH})_4^{2-}]/[\text{Hg}(\text{OH})_3^-][\text{OH}^-], \quad (4-121)$$

for which  $\log K_{f2}$ ,  $\log K_{f3}$ , and  $\log K_{f4}$  are 11.2, -0.9, and -2.0, respectively. The equilibria as acid dissociations are:



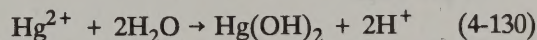
$$K_{a1} = [\text{Hg}(\text{OH})^+][\text{H}^+]/[\text{Hg}^{2+}] \quad (4-126)$$

$$K_{a2} = [\text{Hg}(\text{OH})_2][\text{H}^+]/[\text{Hg}(\text{OH})^+] \quad (4-127)$$

$$K_{a3} = [\text{Hg}(\text{OH})_3^-][\text{H}^+]/[\text{Hg}(\text{OH})_2] \quad (4-128)$$

$$K_{a4} = [\text{Hg}(\text{OH})_4^{2-}][\text{H}^+]/[\text{Hg}(\text{OH})_3^-], \quad (4-129)$$

for which  $\log K_{a1} = -3.4$ ,  $\log K_{a2} = -2.8$ ,  $\log K_{a3} = -14.9$ , and  $\log K_{a4} = -16.0$ . This series of  $\log K_a$  is not monotonic, with the result that  $\text{Hg}(\text{OH})^+$  never appears on any EPAD. Therefore equations 4-122, 4-123, 4-126, and 4-127 are combined to give



$$K_{a12} = [\text{Hg}(\text{OH})_2][\text{H}^+]^2/[\text{Hg}^{2+}], \quad (4-131)$$

with  $\log K_{a12} = -6.2$ . The pH values  $6.2/2 = 3.1$ , 14.9, and 16.0 divide the respective predominance areas of  $\text{Hg}^{2+}$ ,  $\text{Hg}(\text{OH})_2$ ,  $\text{Hg}(\text{OH})_3^-$ , and  $\text{Hg}(\text{OH})_4^{2-}$ . In this case,  $\text{Hg}(\text{OH})_3^-$  and  $\text{Hg}(\text{OH})_4^{2-}$  predominate at  $\text{pH} > 14$ , and would not usually be shown on EPAD.

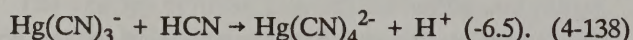
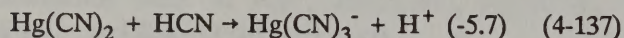
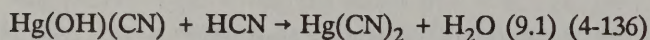
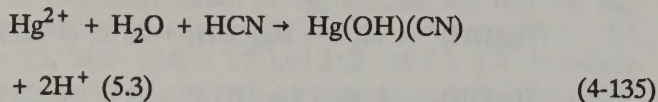
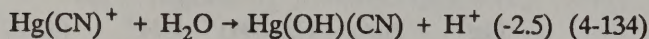
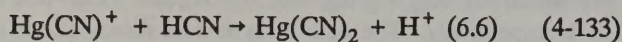
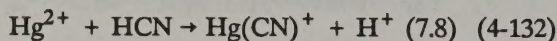
In summary,  $\text{Hg}^{2+}$  predominates at  $\text{pH} < 3.1$ , and  $\text{Hg}(\text{OH})_2$  at  $\text{pH} > 3.1$ ; HCN predominates at  $\text{pH} < 9.2$ , and  $\text{CN}^-$  at  $\text{pH} > 9.2$ . Hence, all of the EPAD are divided into three regions: (1)  $\text{pH} < 3.1$ , where  $\text{Hg}^{2+}$  and HCN predominate, (2)  $3.1 < \text{pH} < 9.2$ , where  $\text{Hg}(\text{OH})_2$  and HCN predominate, and (3)  $\text{pH} > 9.2$ , where  $\text{Hg}(\text{OH})_2$  and  $\text{CN}^-$  predominate.

To proceed further, the complex-formation equilibria in equations 4-92, 4-96, 4-100 through 4-105, 4-130, and 4-131 are rewritten in terms of the predominant uncomplexed metal and free ligand species in each region. This is a straightforward but time-consuming procedure. The system also contains the species  $\text{Hg}(\text{OH})(\text{CN})$  and

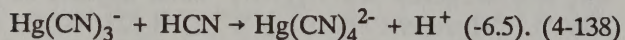
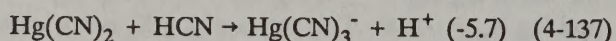
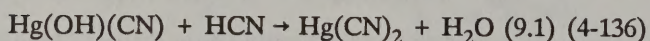
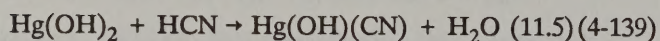


$\text{Hg(OH)(CN)}_2^-$  (table D-5). The equilibria are, with their log K values in parentheses,

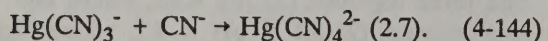
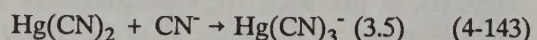
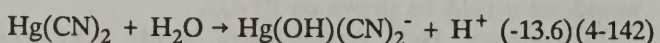
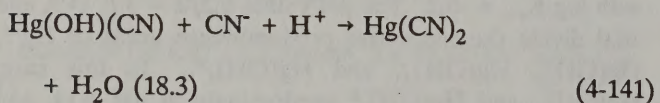
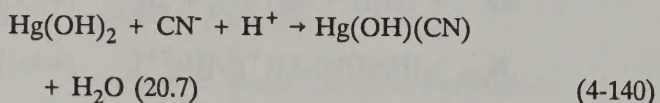
At pH < 3.1:



At  $3.1 < \text{pH} < 9.2$ :



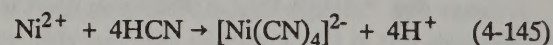
At pH > 9.2:



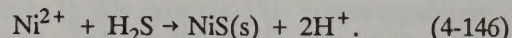
Note that many of equations 4-132 through 4-144 involve  $\text{H}^+$ , so that the corresponding predominance area boundaries are pH dependent. Generation of EPAD from these equilibria manually is a time-consuming procedure that involves trial-and-error calculations. Accordingly, EPAD of complex systems such as this are preferably calculated via computer programs. The EPAD for the  $\text{Hg}^{2+}$ -CN $^-$  system are illustrated in figures E-54 through E-73, some of which include other ligands.

### Example 6: Generation of Additional EPAD

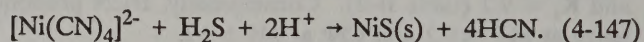
Often an EPAD is desired for a solution composition different from the compositions for which EPAD are provided. As an example, consider the reaction of  $[\text{Ni(C-N)}_4]^{2-}$  with  $\text{SH}^-$ - $\text{H}_2\text{S}$ . Figure E-149 is an EPAD for this system at  $\text{pCN} = -\log a(\text{free cyanide}) = 2.0$  and  $\text{pS} = -\log a(\text{free sulfide}) = 6.0$ . Suppose one is interested in the  $[\text{Ni(CN)}_4]^{2-}$ -NiS(s) boundary at other solution compositions. The equation for that boundary is given by the difference of the formation reactions for the predominant Ni species along it. In the pH range of interest,  $\text{pH} < 7$ , the predominant ligand species are HCN and  $\text{H}_2\text{S}$ . Therefore, the formation reactions are



and



The reaction for the  $[\text{Ni(CN)}_4]^{2-}$ -NiS(s) boundary is the difference of reactions 4-145 and 4-146, namely,



From the Gibbs energy data in tables B-1, C-1, and D-11, or the log K data in tables B-2 and D-11, log K for reaction 4-147 is +9.7. The equation for the  $[\text{Ni(CN)}_4]^{2-}$ -NiS(s) boundary is

$$-4\text{pCN} + \text{pS} + 2\text{pH} - \log a(\text{Ni}) = 9.7, \quad (4-148)$$

recalling equation 4-11 and the definitions of the composition variables for EPAD described in a previous section of this chapter. The slope of equation 4-148 is +2 pH units per unit of log  $a(\text{Ni})$ . With  $\text{pCN} = 2.0$  and  $\text{pS} = 6.0$ ,  $\text{pH} = 5.85$  at  $\log a(\text{Ni}) = 0.0$ , which checks with figure E-149. With  $\text{pCN} = 2.0$  and  $\text{pS} = 4.0$ ,  $\text{pH} = 6.85$  at  $\log a(\text{Ni}) = 0.0$ , and the  $[\text{Ni(CN)}_4]^{2-}$ -NiS(s) boundary is shifted 1.0 pH units to the right. Equation 4-148 also shows that at a given pH,  $a(\text{Ni})$  is lowered 1 unit for every 1 unit of increase of pS. In other words, if the  $\text{H}_2\text{S}$  concentration is raised by a factor of 10, the nickel solubility drops by a factor of 10, at constant pH.

If in equation 4-148 a different value of pCN were considered, a similar calculation would ensue. However, in this case, as shown by comparing figures E-141 through E-145 with figure E-149,  $\text{Ni(CN)}_2(\text{s})$  must be considered. This calls for an equation for the  $\text{Ni(CN)}_2(\text{s})$ -NiS(s) boundary, which may be constructed as in the foregoing discussion. Consequently, the reaction of interest may be the conversion of  $\text{Ni(CN)}_2(\text{s})$  to NiS(s) instead of reaction 4-147.



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## CHAPTER 5.—ULTRAVIOLET AND VISIBLE SPECTRA

### INTRODUCTION

Sunlight plays an important role in the degradation of cyanide and metal cyanide species because photochemical reactions are involved. The extent to which a chemical species undergoes photochemical reactions depends on how much light is absorbed by the species at given wavelengths and how the species reacts upon absorption of light. Many metal cyanide species absorb light in the wavelength range 300 to 450 nm (near ultraviolet to blue), and solar radiation in this wavelength range reaches the Earth's surface (1).<sup>1</sup> Many metal cyanide species absorb ultraviolet light of wavelengths shorter than 300 nm, but solar radiation in this wavelength range is absorbed by the ozone layer and does not reach the Earth's surface (1).

### ABSORPTION OF LIGHT BY CHEMICAL SPECIES

The absorption of light by a chemical species is determined by measuring its absorption spectrum with a spectrophotometer. The relationship of measured quantities is

$$A = \epsilon cl, \quad (5-1)$$

where  $A$  = absorbance, dimensionless,

$\epsilon$  = molar absorptivity,  $(\text{mol L}^{-1})^{-1} \cdot \text{cm}^{-1}$ ,

$c$  = molar concentration,  $M$  ( $\text{mol} \cdot \text{L}^{-1}$ ),

and  $l$  = absorption path length, cm.

The quantity  $\epsilon$  depends on the species, solvent, and light wavelength. The dependence of  $\epsilon$  on temperature is usually slight. If  $\epsilon$  is independent of  $c$ , equation 5-1 expresses the well-known Lambert-Beer law. This is normally the case when  $\epsilon$  pertains to a single species.

The absorbance  $A$  is related to the fraction of light transmitted by

$$\text{pct } T = 100(I/I_0) = 100e^{-A}, \quad (5-2)$$

where  $\text{pct } T$  = percent of light transmitted,

$I$  = transmitted light intensity,

and  $I_0$  = incident light intensity.

Some representative values of  $A$  and  $\text{pct } T$  are

$A$ . . . . .	3.0	2.0	1.0	0.1	0.01	0.001
$\text{pct } T$ . . . .	5.0	13.5	36.8	90.5	99.0	99.9

In a mixture of  $n$  light-absorbing species,

$$A = l(\epsilon_1 c_1 + \epsilon_2 c_2 + \dots + \epsilon_n c_n). \quad (5-3)$$

The fraction of light absorbed by the  $i$ th species is proportional to  $\epsilon_i c_i$ .

Light of shorter wavelengths is as a rule more strongly absorbed, and is absorbed by many more chemical species, than is light of longer wavelengths. Many chemical species are pale yellow or colorless because they absorb little or no visible light, yet they strongly absorb ultraviolet light. The practical lower wavelength limit for obtaining ultraviolet absorption data is 180 to 200 nm because oxygen, water, and the fused-quartz sample containers absorb light at shorter wavelengths.

For many chemical species that absorb light, the absorption spectrum is characterized by maximum absorptions at certain wavelengths. On either side of the absorption maximum, absorbance decreases over a range of wavelengths. The shapes of these absorption curves, termed "bands," approximate Gaussian (bell-shaped) curves. Often multiple absorption bands occur, and the respective bands are superimposed. The result of superimposition of absorption bands is often the obliteration of absorption maxima, and the absorption spectrum consists of steeply increasing absorption with decreasing wavelength.

### DATA PRESENTATION

This chapter contains a compilation of ultraviolet and visible spectroscopic data for cyanide and derived species, metal cyanide complexes, and auxiliary species. It is important to know the molar absorptivities at 300 to 450 nm for auxiliary species and species derived from cyanide in order to assess their interference with photochemical cyanide destruction.

In the literature, spectra are reported as functions of wavelength  $L$ , wave number  $k$ , or more rarely frequency  $\nu$ . These quantities are related to each other and the speed of light  $c$ :

$$k = 1/L, \quad (5-4)$$

$$c = L\nu = \nu/k. \quad (5-5)$$

<sup>1</sup>Italic numbers in parentheses refer to items in the list of references at the end of this chapter.



In this publication, all visible-ultraviolet spectral data are tabulated with respect to wavelength  $L$ .

Literature sources for spectroscopic data often quote only absorption maxima and do not show the complete spectra. This practice is more frequent in the more recent literature. However, the complete spectra are needed to evaluate the contribution of species to light absorption in a range of wavelengths. Accordingly, most of the references cited on the tables in this chapter report complete spectra. In this chapter, the molar absorptivities are tabulated at the absorption maxima and at selected wavelengths. The selected wavelengths are 400, 350, and 300 nm, which cover the range of wavelengths of solar ultraviolet light reaching the Earth's surface. Often the molar absorptivity varies greatly with wavelength at wavelengths other than at maximum molar absorptivity. The variation of molar absorptivity can exceed 20 pct per nanometer. Consequently, most of the molar absorptivities quoted at the selected wavelengths are approximate and often given to only one significant figure.

### FREE CYANIDE AND DERIVED SPECIES

Ultraviolet and visible spectroscopic data for free cyanide and derived species in aqueous solution are compiled in table 5-1. The species are arranged in the same order as in the tables in chapter 2. Nearly all derived species are colorless, with absorptions at wavelengths  $<400$  nm; some species, including HCN and  $\text{CN}^-$ , are transparent to 200-220 nm. All of the data are from primary sources (2-30), which give complete spectra for the majority of the most important derived species. For many other auxiliary species, the sources quote only absorption maxima and do not show complete spectra. However, the derived species that are the strongest near-ultraviolet absorbers, 300 to 400 nm, are easily oxidized sulfur compounds that are not expected to occur at significant concentrations; see chapter 7.

### METAL CYANIDE SPECIES

Ultraviolet and visible spectroscopic data for metal cyanide species are compiled in table 5-2. The spectra of the metal complexes differ greatly, depending on the metal, its oxidation state, and the composition of the complex. Most of the data are available in Sharpe's monograph (31). Primary sources were consulted for more recent data and complete spectra (32-57).

The cyanide complexes of Zn, Cd, and Hg are colorless and are transparent to below 300 nm, so none of them absorb sunlight. The cyanide complexes of Cu(I), Ag, and Au(I) are all colorless, but have strong ultraviolet absorption maxima. Only the copper complexes absorb significantly at 300 to 350 nm.

The cyanide complexes of Ni(II) and Co(III) are generally yellow and absorb in the blue through the ultraviolet. Nothing is known about dinuclear Co(III) cyanide complexes.

Spectra have been published for several mononuclear and dinuclear iron cyanide complexes. Iron is the most abundant accessory element in precious metals mining, and its cyanide complexes are the strongest ultraviolet absorbers among metal cyanide species. This fact is important for the photochemical degradation of iron cyanide species, which is discussed in chapter 9. Generally there are few or no data for wavelengths below 300 to 350 nm. The mononuclear complexes are all different shades of yellow; the dinuclear complexes have different colors. The data for the dinuclear complexes are approximate, and the molar absorptivities are uncertain by as much as a factor of 2. The data from references 51, 52, and 54 are entered in table 5.2 because in those references spectra for related species were reported, and their relative molar absorptivities are probably reliable.

The spectral data for manganese cyanide complexes are inadequate and do not agree (31); this is attributed to their instability in the absence of excess  $\text{CN}^-$ . There are no more recent reliable data. The tabulated Cr(III) cyanide complexes are yellow. The vanadium cyanide complexes are known to exist in complex equilibria in aqueous solution (58), and reliable spectra of pure species have not been reported.

Further details of the chemistry of metal cyanide complexes are discussed in chapter 8. The spectra of the Fe, Co, and Cr cyanide complexes are important for their photochemical destruction; see chapter 9.

### AUXILIARY SPECIES

Table 5-3 compiles spectroscopic data for auxiliary species (3, 59-86). Most of the oxoanions and their acids do not show absorption maxima at wavelengths above 200 nm. In most cases, complete spectra were located.

Many of the tabulated auxiliary species are oxidants that might be used to destroy cyanides, as well as the species to which these oxidants are thus reduced. These include  $\text{O}_3$ ,  $\text{H}_2\text{O}_2/\text{HO}_2$ , and species containing chlorine or bromine. The halate ions  $\text{ClO}_3^-$  and  $\text{BrO}_3^-$  form during decomposition of the hypohalites or  $\text{ClO}_2$  and  $\text{ClO}_2^-$ . No spectra of the peroxomonosulfate species  $\text{HSO}_5^-$  and  $\text{SO}_5^{2-}$ , the presumed intermediates in  $\text{SO}_2$ -air oxidation processes, were located. The spectra of  $\text{SO}_2$  and sulfites are also included. Most of the oxidant species just mentioned absorb in the 300- to 350-nm range.

Other auxiliary species, such as S, Se, P, and As species, are derived from the leaching of accessory minerals. The polysulfides,  $\text{S}_n^{2-}$ , form when sulfur dissolves in sulfide solutions; they are stable only in a very narrow range of



Table 5-1.-Ultraviolet-visible spectroscopic data for free cyanide and derived species in aqueous solution

Species	Wave-length, maximum, nm	Molar absorptivity, <sup>1,2</sup> (mol L <sup>-1</sup> ) <sup>-1</sup> cm <sup>-1</sup>				References
		Maximum	300 nm	350 nm	400 nm	
C(II):						
HCN	<sup>3</sup> <200	N	<0.1	<0.1	<0.1	2
CN <sup>-</sup>	170	N	<.1	<.1	<.1	3, 4
H-CS-NH <sub>2</sub>	<sup>4</sup> 263	1.25E4	N	N	N	5
H-CS <sub>2</sub> <sup>-</sup>	386	8.4 E4	N	N	N	6
	331	9.6 E6				
	225	2.9 E6				
H-CO-NH <sub>2</sub>	189	8. E6	N	N	N	2, 7
H-COS <sup>-</sup>	246	8.6 E6	N	N	N	6
	208	5.5 E6				
H-CO <sub>2</sub> H	208	4.6 E1	<.1	<.1	<.1	8, 9
H-CO <sub>2</sub> <sup>-</sup>	205	1.00E2	<.1	<.1	<.1	9
C(III):						
NC-CN	222	1.1 E1	<.1	<.1	<.1	10
	211	3.7 E1				
	201	6.0 E1				
NC-CS-NH <sub>2</sub>	<sup>5</sup> 438	3.2 E1	N	N	N	11
	294	7.4 E3				
NC-CO-NH <sub>2</sub>	206	3.47E3	<1?	<.1?	<.1?	10
NC-CO-NH <sup>-</sup>	220	5.12E3	<10?	<.1?	<.1?	10
H <sub>2</sub> N-CS-CS-NH <sub>2</sub>	<sup>6</sup> 483	2.2 E1	1.0E4	3. E3	8. E1	12
	312	1.12E4				
C <sub>2</sub> S <sub>4</sub> <sup>2-</sup>	<sup>4</sup> 342	N	N	N	N	13
	278					
H <sub>2</sub> N-CS-CO-NH <sub>2</sub>	<sup>6</sup> 411	2.9 E1	7. E3	1.2E2	3. E1	12
	301	6.6 E3				
	229	4.6 E3				
H <sub>2</sub> N-CO-CO-NH <sub>2</sub>	202	8.3 E3	<1?	<.1?	<.1?	10
H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	<200	N	<.1	<.1	<.1	14
HC <sub>2</sub> O <sub>4</sub> <sup>-</sup>	<200	N	<.1	<.1	<.1	14
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	<200	N	<.1	<.1	<.1	14



Table 5-1.-Ultraviolet-visible spectroscopic data for free cyanide and derived species in aqueous solution-Continued

Species	Wave-length, maximum, nm	Molar absorptivity, <sup>1,2</sup> (mol L <sup>-1</sup> ) <sup>-1</sup> cm <sup>-1</sup>				References
		Maximum	300 nm	350 nm	400 nm	
C(IV):						
ClCN	<sup>3</sup> 179	N	N	N	N	15, 16
BrCN	<sup>3</sup> 202	N	N	N	N	15, 16
NCNH <sub>2</sub>	<200	N	<1?	<.1?	<.1?	17, 18
NCNH <sup>-</sup>	<200	N	<1?	<.1?	<.1?	
NCS <sup>-</sup>	216 187	3.4 E3 N	<.1	<.1	<.1	4, 19, 20, 21
NCSe <sup>-</sup>	235 211 183	3.7 E3 N N	<1?	<.1	<.1	4, 19
NCO <sup>-</sup>	194	1.0 E3	<.1	<.1	<.1	4, 22, 23
HNC(NH <sub>2</sub> ) <sub>2</sub>	<200	N	<.1	<.1	<.1	17
C(NH <sub>2</sub> ) <sub>3</sub> <sup>+</sup>	<200	N	<.1	<.1	<.1	17
CS(NH <sub>2</sub> ) <sub>2</sub>	235 194	1.3 E4 1.1 E4	N	N	N	24
H <sub>2</sub> NCS <sub>2</sub> <sup>-</sup>			N	N	N	25, 26
CS <sub>3</sub> <sup>2-</sup>	400 336 223	3. E1 1. E4 1. E4	N	N	N	27, 28
CO(NH <sub>2</sub> ) <sub>2</sub>	189	1.5 E3	<.1	<.1	<.1	7, 17
H <sub>2</sub> NCOS <sup>-</sup>	225	5.2 E4	N	N	N	29
COS <sub>2</sub> <sup>2-</sup>	272	N	N	N	N	28
CO <sub>3</sub> <sup>2-</sup>	<200	N	<.1	<.1	<.1	27, 28
CNO <sup>-</sup>	<sup>4</sup> 280	5. E1	4. E1	5.	<1?	30

N No data.

<sup>1</sup>En = 10<sup>n</sup>, e.g. 1.25E4 = 1.25×10<sup>4</sup>.

<sup>2</sup>Question marks denote uncertain values due mainly to long extrapolations.

<sup>3</sup>Gas.

<sup>4</sup>In methanol.

<sup>5</sup>In dichloromethane-heptane.

<sup>6</sup>In ethanol.



Table 5-2.-Ultraviolet-visible spectroscopic data for  
metal cyanide species in aqueous solution

Species	Wave-length, maximum, nm	Molar absorptivity, <sup>1</sup> (mol L <sup>-1</sup> ) <sup>-1</sup> cm <sup>-1</sup>				Additional references
		Maximum	300 nm	350 nm	400 nm	
Zn(CN) <sub>4</sub> <sup>2-</sup>	<200	N	<0.1	<0.1	<0.1	32
Cd(CN) <sub>4</sub> <sup>2-</sup>	<200	N	<.1	<.1	<.1	32
Hg(CN) <sub>2</sub>	<200	N	<.1	<.1	<.1	33
Hg(CN) <sub>3</sub> <sup>-</sup>	<200	N	N	N	N	
Hg(CN) <sub>4</sub> <sup>2-</sup>	<200	N	<.1	<.1	<.1	32
Cu(CN) <sub>2</sub> <sup>-</sup>	234	1.1 E4	1. E2	<1	<.1	33, 34, 35
	222	1.1 E4				
	209	2.0 E4				
Cu(CN) <sub>3</sub> <sup>2-</sup>	238	1.1 E4	1. E2	<1	<.1	34, 35
	202	2.0 E4				
Cu(CN) <sub>4</sub> <sup>3-</sup>	235	1.1 E4	1. E2	<1	<.1	34, 35
	206	2.0 E4				
Ag(CN) <sub>2</sub> <sup>-</sup>	196	2.1 E4	<1	<.1	<.1	33, 36
Ag(CN) <sub>3</sub> <sup>2-</sup>	N	N	N	N	N	
Ag(CN) <sub>4</sub> <sup>3-</sup>	N	N	N	N	N	
Au(CN) <sub>2</sub> <sup>-</sup>	240	3.3 E3	<1	<.1	<.1	33, 36
	230	3.6 E3				
	211	1.0 E4				
	205	1.2 E4				
Au(CN) <sub>4</sub> <sup>-</sup>	<200	N	<1	<.1	<.1	37
Ni(CN) <sub>4</sub> <sup>2-</sup>	310	7.0 E2	6. E2	1.8E2	5.	32, 36, 38
	286	4.4 E3				
	268	1.2 E4				
Co(CN) <sub>6</sub> <sup>3-</sup>	313	1.9 E2	1.6E2	3. E1	.5	39, 40, 41
	260	1.4 E2				
Co(H <sub>2</sub> O)(CN) <sub>5</sub> <sup>2-</sup>	380	2.8 E2	1.0E2	1.5E2	2.0E2	40, 41, 42
	280	1.0 E2				
Co(OH)(CN) <sub>5</sub> <sup>3-</sup>	375	2.4 E2	2.0E2	1.7E2	1.6E2	42
	288	2.4 E2				
Fe(CN) <sub>6</sub> <sup>4-</sup>	322	3.1 E2	4. E2	1.6E2	5.	43, 44, 45
	218	2.3 E4				



Table 5-2.-Ultraviolet-visible spectroscopic data for metal cyanide species in aqueous solution—Continued

Species	Wave-length, maximum, nm	Molar absorptivity, <sup>1</sup> (mol L <sup>-1</sup> ) <sup>-1</sup> cm <sup>-1</sup>				Additional references
		Maximum	300 nm	350 nm	400 nm	
Fe(CN) <sub>6</sub> <sup>3-</sup>	420 302	1.0 E3 1.6 E3	1.6E3	3.3E2	9. E2	43, 45
Fe(H <sub>2</sub> O)(CN) <sub>5</sub> <sup>3-</sup>	440	6.5 E2	5. E2	1.8E2	3.5E2	46, 47, 48, 49
Fe(H <sub>2</sub> O)(CN) <sub>5</sub> <sup>2-</sup>	395 340	7.4 E2 7.5 E2	9. E2	7. E2	7. E2	45, 49, 50
Fe(OH)(CN) <sub>5</sub> <sup>3-</sup>	390	1.6 E3	7. E2	9. E2	1.6E3	45, 50
Fe <sub>2</sub> (CN) <sub>11</sub> <sup>7-</sup>	380 315	8. E2 1.6 E3	1.7E3	1.0E3	7. E2	51
Fe <sub>2</sub> (CN) <sub>11</sub> <sup>6-</sup>	1300	3. E3	3. E3	1.6E3	1.1E3	51
Fe <sub>2</sub> (CN) <sub>11</sub> <sup>5-</sup>	560 400 295	8. E2 2. E3 4.5 E3	4. E3	2. E3	2. E3	51
Fe <sub>2</sub> (CN) <sub>10</sub> <sup>6-</sup>	390	1.0 E3	1.0E3	8. E2	9. E2	48, 52, 53
Fe <sub>2</sub> (CN) <sub>10</sub> <sup>5-</sup>	1280 390 350	6. E3 1.7 E3 1.7 E3	3. E3	1.7E3	1.6E3	52
Fe <sub>2</sub> (CN) <sub>10</sub> <sup>4-</sup>	560 400 360	2.7 E3 2.5 E3 2.5 E3	4. E3	2.4E3	2.5E3	45, 50, 52, 54, 55
Fe <sub>2</sub> (H <sub>2</sub> O)(CN) <sub>10</sub> <sup>6-</sup>	N	N				
Fe <sub>2</sub> (H <sub>2</sub> O)(CN) <sub>10</sub> <sup>5-</sup>	>1000 400	>1. E3 2. E3	N	N	2. E3	55
Fe <sub>2</sub> (H <sub>2</sub> O)(CN) <sub>10</sub> <sup>4-</sup>	525 400	1.1 E3 2. E3	N	N	2. E3	55
Fe <sub>2</sub> (OH)(CN) <sub>10</sub> <sup>5-</sup>	610	6. E2	N	N	3. E3	55
Cr(CN) <sub>6</sub> <sup>3-</sup>	377 307	8.6 E1 6.0 E1	5. E1	4. E1	6. E1	56
Cr(H <sub>2</sub> O)(CN) <sub>5</sub> <sup>2-</sup>	405 320	1.1 E2 5. E1	4. E1	5. E1	1.1E2	57
Cr(OH)(CN) <sub>5</sub> <sup>3-</sup>	415 355	1.2 E2 8. E1	3. E1	8. E1	1.1E2	57

N No data.

<sup>1</sup>En = 10<sup>n</sup>, e.g., 1.1 E4 = 1.1×10<sup>4</sup>.



Table 5-3.-Ultraviolet-visible spectroscopic data for auxiliary species in aqueous solution

Species	Wave-length, maximum, nm	Molar absorptivity, <sup>1,2</sup> (mol L <sup>-1</sup> ) <sup>-1</sup> cm <sup>-1</sup>				References
		Maximum	300 nm	350 nm	400 nm	
O <sub>3</sub>	260	3.3 E3	N	N	N	59
OH <sup>-</sup>	<200	N	<0.1	<0.1	<0.1	60
H <sub>2</sub> O <sub>2</sub>	<200	N	1.0	<.1	<.1	61
HO <sub>2</sub> <sup>-</sup>	<200	N	2.7E1	1.	<.1	61
Cl <sub>2</sub>	324	7.7 E1	5. E1	4. E1	3.	62, 63
Cl <sup>-</sup>	<200	N	<.1	<.1	<.1	64
HClO	233	9.7 E1	2.4E1	2.2E1	.2	62, 65, 66
ClO <sup>-</sup>	292	3.5 E2	3.2E2	2. E1	.5	65, 66
ClO <sub>2</sub> <sup>-</sup>	260	1.49E2	7. E1	2.	.1	67
ClO <sub>2</sub> <sup>-</sup>	360	1.20E3	1.2E3	3. E2	6. E2	67
ClO <sub>3</sub> <sup>-</sup>	<200	N	<.1	<.1	<.1	3, 68
Br <sub>2</sub>	390	1.5 E2	8.	7. E1	1.5E2	63, 69
Br <sup>-</sup>	<200	N	<.1?	<.1	<.1	70
HBrO	262	9. E1	5. E1	3. E1	1. E1	66, 69, 71
BrO <sup>-</sup>	329	3.5 E2	1.6E2	2.5E2	5.	66, 69, 71, 72
BrO <sub>3</sub> <sup>-</sup>	<200	N	<.1?	<.1	<.1	3, 68, 72
H <sub>2</sub> S	<200	N	<.1?	<.1	<.1	73
SH <sup>-</sup>	230	7.1 E3	5.	<.1?	<.1	74, 75
S <sub>2</sub> <sup>2-</sup>	358	8.5 E2	3. E2	8. E2	1.8E2	76
S <sub>3</sub> <sup>2-</sup>	417	9.5 E1	1.2E3	9. E1	8. E1	76
	303	1.14E3				
S <sub>4</sub> <sup>2-</sup>	368	3.2 E2	1.2E3	3. E2	1.8E2	76
	303	1.14E3				
S <sub>5</sub> <sup>2-</sup>	375	6.4 E2	2.0E3	7. E2	5. E2	76
	299	2.0 E3				
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	215	3.7 E3	.4	<.1	<.1	3, 77, 78
SO <sub>2</sub>	276	5.0 E2	1.8E2	<.1?	<.1	78, 79
HSO <sub>3</sub> <sup>-</sup>	<200	N	<.1	<.1	<.1	78, 80
S <sub>2</sub> O <sub>5</sub> <sup>2-</sup>	255	2.6 E3	1.1E2	<.1?	<.1	78, 80
SO <sub>3</sub> <sup>2-</sup>	<200	N	<.1	<.1	<.1	3, 80
SO <sub>4</sub> <sup>2-</sup>	<200	N	<.1	<.1	<.1	3
H <sub>2</sub> SeO <sub>3</sub>	<sup>3</sup> <200	N	<.1	<.1	<.1	81
HSeO <sub>3</sub> <sup>-</sup>	<200	N	<.1	<.1	<.1	81
SeO <sub>3</sub> <sup>2-</sup>	<200	N	<.1	<.1	<.1	81
SeO <sub>4</sub> <sup>2-</sup>	<200	N	<.1	<.1	<.1	81
NH <sub>3</sub>	<200	N	<.1	<.1	<.1	73
NH <sub>4</sub> <sup>+</sup>	<200	N	<.1	<.1	<.1	82
NH <sub>2</sub> Cl	<sup>4</sup> 243	4.6 E2	6.	<.1	<.1	66, 83, 84
NH <sub>2</sub> Br	<sup>5</sup> 278	3.8 E2	2.3E2	3.	<.1?	66, 69, 71
NO <sub>2</sub> <sup>-</sup>	355	2.2 E1	9.	2.1 E	1.	3, 84, 85
	210	5.4 E3				
NO <sub>3</sub> <sup>-</sup>	301	7.1	7.0	<.1	<.1	3, 84, 86
	200	1.0 E4				



Table 5-3.-Ultraviolet-visible spectroscopic data for auxiliary species in aqueous solution—Continued

Species	Wave-length, maximum, nm	Molar absorptivity, <sup>1,2</sup> (mol L <sup>-1</sup> ) <sup>-1</sup> cm <sup>-1</sup>				References
		Maximum	300 nm	350 nm	400 nm	
H <sub>3</sub> PO <sub>4</sub>	<200	N	<.1	<.1	<.1	3
H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	<sup>6</sup> <200	N	<.1	<.1	<.1	
HPO <sub>4</sub> <sup>2-</sup>	<200	N	<.1	<.1	<.1	60
PO <sub>4</sub> <sup>3-</sup>	<200	N	<.1	<.1	<.1	60
H <sub>3</sub> AsO <sub>3</sub>	<sup>7</sup> <200	N	<.1	<.1	<.1	
H <sub>2</sub> AsO <sub>3</sub> <sup>-</sup>	<sup>7</sup> <200	N	<.1	<.1	<.1	
HAsO <sub>3</sub> <sup>2-</sup>	<sup>7</sup> <200	N	<.1	<.1	<.1	
H <sub>3</sub> AsO <sub>4</sub>	<sup>8</sup> <200	N	<.1	<.1	<.1	
H <sub>2</sub> AsO <sub>4</sub> <sup>-</sup>	<sup>8</sup> <200	N	<.1	<.1	<.1	
HAsO <sub>4</sub> <sup>2-</sup>	<sup>8</sup> <200	N	<.1	<.1	<.1	
AsO <sub>4</sub> <sup>3-</sup>	<sup>8</sup> <200	N	<.1	<.1	<.1	

N No data.

<sup>1</sup>En = 10<sup>3</sup>, e.g., 3.3 E3 = 3.339×10<sup>3</sup>.

<sup>2</sup>Question marks denote uncertainty due to long extrapolation.

<sup>3</sup>All data estimated from trend of data for SeO<sub>3</sub><sup>2-</sup> and HSeO<sub>3</sub><sup>-</sup>.

<sup>4</sup>The cited references also give data for NHCl<sub>2</sub> and NCl<sub>3</sub>.

<sup>5</sup>The cited references also give data for NHBr<sub>2</sub> and NBr<sub>3</sub>.

<sup>6</sup>All data estimated from data for H<sub>3</sub>PO<sub>4</sub>, HPO<sub>4</sub><sup>2-</sup>, and PO<sub>4</sub><sup>3-</sup> in references 3 and 60.

<sup>7</sup>All data estimated from data for HPO<sub>3</sub><sup>2-</sup> in reference 3 and data for S(IV) and Se(IV) species in references 78-81.

<sup>8</sup>All data estimated from data for SeO<sub>4</sub><sup>2-</sup> versus SO<sub>4</sub><sup>2-</sup> and data for corresponding P(V) species, in references 3, 60, and 81.

pH and Eh in the absence of cyanides. Selenide and polyselenide species are not included; they are very easily oxidized by air. Phosphorus species are rare in the context of precious metals mining; the data for them were used to predict data for arsenic species, for which no data were located. Except for the polysulfides, the tabulated S, Se, P, and As species absorb only at wavelengths below 300 nm.

Inorganic nitrogen species that may form during cyanide oxidation are also included. These consist primarily of NH<sub>3</sub>/NH<sub>4</sub><sup>+</sup>, N<sub>2</sub>, NO<sub>2</sub><sup>-</sup>, and NO<sub>3</sub><sup>-</sup>. The haloamines NH<sub>2</sub>Cl and NH<sub>2</sub>Br form when NH<sub>3</sub> reacts with hypohalites. The species NH<sub>3</sub>/NH<sub>4</sub><sup>+</sup> are transparent at wavelengths above 200 nm. The other nitrogen species absorb weakly at 300 to 400 nm.

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## CHAPTER 6.—INFRARED SPECTRA

### INTRODUCTION

Infrared spectra result from the absorption of light at wavelengths corresponding to molecular vibrations. Absorption maxima are commonly quoted in units of reciprocal wavelength centimeters. The absorption maxima are usually sharp and narrow and are commonly referred to as "absorption frequencies" in the literature.

Cyanide in the form of free or complexed cyanide, or the CN group in derived species such as  $\text{ClCN}$ ,  $\text{NCO}^-$ , or  $\text{SCN}^-$ , or in organic nitriles such as  $\text{CH}_3\text{CN}$  absorbs strongly in the region around  $2,000\text{ cm}^{-1}$ . Water absorbs over large wavelength regions of the infrared spectrum, but it is transparent in the region around  $2,000\text{ cm}^{-1}$ , where absorption due to the vibration of the CN group occurs. Infrared spectra are therefore useful for detecting and identifying solid, gaseous, or aqueous species that contain the CN group.

This chapter contains a compilation of infrared spectroscopic data for the CN vibration in cyanide and derived species and in metal cyanide species.

### FREE CYANIDE AND DERIVED SPECIES

Free cyanide and derived species show infrared maxima near  $2,000\text{ cm}^{-1}$ . Data for these species are compiled in table 6-1. A major reference for infrared spectra of inorganic species is Nakamoto's compilation (1),<sup>1</sup> from which most of the data in table 6-1 were obtained. Data are also given for gaseous molecules and for ions in solid potassium salts for comparison with the aqueous solution data. These data presumably approximate spectra that are unknown for species in aqueous solution. Additional data were obtained from primary sources (2-7).

### METAL CYANIDE SPECIES

Data for metal cyanide complexes are compiled in table 6-2. All of the data were taken from Nakamoto (1) and Sharpe (8). The molar absorption coefficients differ greatly and depend mainly on molecular structure. There are very few data for dinuclear cyanide complexes, e.g. of iron, or for cyanide complexes that contain other ligands

such as  $\text{H}_2\text{O}$  or  $\text{OH}^-$ . Data for solid compounds can also be found in Nakamoto (1) and Sharpe (8). In solid compounds more than one CN infrared absorption frequency often occurs because of asymmetry effects.

### METAL THIOCYANATE SPECIES

Metal thiocyanate complexes show infrared absorption due to the CN bond at  $2,050$  to  $2,150\text{ cm}^{-1}$  in the solid state (1), so absorption in this region may be expected for the complexes in aqueous solution. However, equilibrium data (appendix D) indicate that thiocyanate complexes of the metals of interest in this publication will not be important. A free thiocyanate concentration of  $0.01M$  to  $0.1M$  is required to form thiocyanate complexes of zinc or cadmium. The thiocyanates of Cu, Ag, and Hg are relatively insoluble, and at a free thiocyanate concentration of  $0.01M$ , the concentrations of metal thiocyanate species in equilibrium with the solid metal thiocyanates would be of the order of  $10^{-4}M$ ,  $10^{-6}M$ , and  $10^{-2}M$ , respectively. However,  $\text{CN}^-$  complexes Cu, Ag, and Hg much more strongly than  $\text{SCN}^-$ , so the concentrations of thiocyanate complexes under process conditions would be insignificant.

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<sup>1</sup>Italic numbers in parentheses refer to items in the list of references at the end of this chapter.



Table 6-1.-Infrared spectroscopic data for free cyanide and derived species

Species	CN absorption				Additional references
	Gas (g) or K salt (s)		Aqueous solution		
	Type	Frequency, $\text{cm}^{-1}$	Frequency, $\text{cm}^{-1}$	Molar absorp- tivity, $\text{cm}^2\text{M}^{-1}$	
HCN	g	2,097	2,095	64	2
CN <sup>-</sup>	s	2,080	2,080	29	2
NC-CN	g	2,065	N	N	3
ClCN	g	2,219	N	N	
BrCN	g	2,200	N	N	
HNCO	g	2,274	N	N	
NCO <sup>-</sup>	s	2,155	N	N	
NCS <sup>-</sup>	s	2,053	2,066	537	4
NCSe <sup>-</sup>	s	2,070	2,075	N	5
HCNO	g	2,198	N	N	6
CNO <sup>-</sup>	s	2,052	2,121 2,052	N N	7

N No data.



Table 6-2.-Infrared spectroscopic data for metal cyanide species in aqueous solution

Species	Frequency, $\text{cm}^{-1}$	Molar absorptivity $\text{cm}^{-1} \text{ M}^{-1}, \times 10^{-3}$
$\text{Zn}(\text{CN})_4^{2-}$	2,149	0.11
$\text{Cd}(\text{CN})_4^{2-}$	2,140	.08
$\text{Hg}(\text{CN})_2^-$	2,194	.003
$\text{Hg}(\text{CN})_3^{2-}$	2,161	.026
$\text{Hg}(\text{CN})_4^{2-}$	2,143	.11
$\text{Cu}(\text{CN})_2^-$	2,125	.16
$\text{Cu}(\text{CN})_3^{2-}$	2,094	1.09
$\text{Cu}(\text{CN})_4^{3-}$	2,076	1.66
$\text{Ag}(\text{CN})_2^-$	2,135	.26
$\text{Ag}(\text{CN})_3^{2-}$	2,105	.38
$\text{Ag}(\text{CN})_4^{3-}$	2,092	.56
$\text{Au}(\text{CN})_2^-$	2,146	N
$\text{Au}(\text{CN})_4^-$	2,189	N
$\text{Ni}(\text{CN})_4^{2-}$	2,124	1.1
$\text{Co}(\text{CN})_6^{3-}$	2,129	N
$\text{Fe}(\text{CN})_6^{4-}$	2,044	N
$\text{Fe}(\text{CN})_6^{3-}$	2,118	N
$\text{Cr}(\text{CN})_6^{3-}$	2,128	N

N No data.



## CHAPTER 7.—REACTIONS OF FREE CYANIDE AND DERIVED SPECIES

### INTRODUCTION

#### General Remarks

The treatment of liquids and solids containing waste cyanide and the fate of  $\text{CN}^-$  in the environment have been the subject of numerous studies and publications. The question of what chemical reactions cyanide undergoes, naturally or artificially, is therefore critical. No recent comprehensive review of the inorganic chemistry of free  $\text{CN}^-$  or species derived therefrom appears to exist. This chapter provides such a review by compiling data on the reactions of free  $\text{CN}^-$  and derived species.

Free  $\text{CN}^-$  is subject to reactions that convert it to products that in turn undergo further reactions. The reaction products are the derived species tabulated in chapter 2. The reactions that occur include oxidation, hydration, reactions with auxiliary species, and hydrolysis. The auxiliary species that may react with cyanide include ammonia ( $\text{NH}_3$ ), sulfides, or species derived from the incomplete oxidation of sulfides. Ammonia is a product of the hydrolysis of  $\text{CN}^-$  and  $\text{NCO}^-$  (cyanate). Sulfides are derived from minerals, and they are subject to oxidation to other sulfur species, which react with free  $\text{CN}^-$ .

The ultimate fate of cyanide carbon in the presence of air is predicted to be  $\text{CO}_2$  or carbonates, according to thermodynamic data. The ultimate fate of cyanide nitrogen depends on the availability of reactive oxidants, and may be  $\text{NH}_3$ ,  $\text{N}_2$ ,  $\text{NO}_2$ , or  $\text{NO}_3^-$ . However, many of the steps in the process leading to the final products are slow, and knowledge of the rates of the intermediate reactions is important.

This chapter contains a brief review of the fundamentals of reaction rates or kinetics, a classification of types of chemical reactions, and a description of the organization of the data that constitute the bulk of this chapter. Most of the data pertain to oxidation, addition, hydrolysis, and exchange reactions of free  $\text{CN}^-$  and derived species. The chemistry of selenium in cyanide solutions is discussed in a subsequent section. Finally, industrial observations on cyanide degradation are discussed.

#### Reaction Rate Fundamentals

##### Thermodynamic Versus Kinetic Control of Chemical Reactions

In chapter 4, it was stated that the extent to which a chemical reaction can proceed is determined by thermodynamics and kinetics. The role of thermodynamics was discussed in chapter 4. If the standard Gibbs energy change

for a chemical reaction is negative, the reaction can proceed. The rate at which the reaction proceeds is determined by kinetics, through the rate constant and the activation parameters, as described below. Practically all of the reactions described in this chapter have negative standard Gibbs energy changes, so the extent to which they proceed is kinetically controlled.

#### Reaction Order and Rate Constant

Reactions proceed in elementary steps that consist of simple reactions involving usually only one or two molecules. This sequence of simple reactions collectively expresses the reaction mechanism. The slowest of these steps, the rate-limiting step, determines the reaction rate. Most reactions consist of more than one elementary step, so that the stoichiometry of the reaction corresponds to the sum of all of the elementary steps, not to any individual step. In most reactions, the rate-limiting step is first or second order. In a first-order reaction, the rate depends directly on the concentration of one reactant species, denoted Z:

$$\text{rate} = -d[\text{Z}]/dt = k[\text{Z}], \quad (7-1)$$

where  $k$  = the rate constant,

and  $[\text{Z}]$  = concentration of reactant species Z.

In a second-order reaction, the rate depends on the concentrations of two reactant species, denoted Z and R, or on the square of the concentration of one reactant:

$$\text{rate} = -d[\text{Z}]/dt = k[\text{Z}][\text{R}] \quad (7-2)$$

$$\text{or} \quad \text{rate} = -d[\text{Z}]/dt = k[\text{Z}]^2. \quad (7-3)$$

In the case represented by equation 7-2, the reaction is first order each in  $[\text{Z}]$  and  $[\text{R}]$ , and second order overall. Equations 7-1 through 7-3 are termed "rate equations." In this publication, most reaction rates conform to equations 7-1 or 7-2. The term "substrate" is applied to the reactant of primary interest, namely cyanide or a derived species, which is denoted Z. Reactants that are reagents are denoted R. Water is often a reactant, but its concentration does not appear in rate equations for reactions in aqueous solution because it is present in very large and constant excess, namely, 50M to 55M. Rate equations are treated further in chapter 12, which is a users' guide for solving reaction rate problems.



## Dependence of Reaction Rates on pH

Reaction rates in aqueous solution usually depend on pH. Reactants are often weak acids or bases that therefore exist as different species depending on the pH. These species have different reactivities. Reactions often proceed faster in acid or alkaline solutions, without consumption of acid or base, and are accordingly termed, respectively, acid or base "catalyzed." Two general references on the subject are Jones (1) and Hammett (2).<sup>1</sup> The dependence of reaction rates on pH is addressed further with examples in chapter 12.

## Dependence of Reaction Rates on Temperature

The rate of a chemical reaction depends on temperature through the activation energy  $\Delta E^*$ . The variation of the rate constant  $k$  with absolute temperature  $T$  depends on  $\Delta E^*$  and is given by

$$k = A \exp(-\Delta E^*/RT). \quad (7-4)$$

Equation 7-4 is the well-known Arrhenius relationship (3). The quantity  $A$  is termed the "preexponential factor," and  $R$  is the gas constant. A larger  $\Delta E^*$  results in a steeper variation of  $k$  with  $T$ .

In the older literature, authors treat their data by equation 7-4. Advances in reaction rate theory have led to an improved equation for expressing the variation of the reaction rate constant with temperature. The recommended equation for fitting experimental data is (3)

$$k = T(k'/h) [\exp(\Delta S^*/R)] [\exp(-\Delta H^*/RT)], \quad (7-5)$$

where  $k$  = rate constant,

$T$  = absolute temperature,

$k'$  = Boltzmann constant,  $1.38066 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$ ,

$h$  = Planck's constant,  $6.626076 \times 10^{-34} \text{ J} \cdot \text{s}$ ,

$k'/h$  =  $2.08367 \times 10^{10} \text{ s} \cdot \text{K}^{-1}$  (4),

$\Delta S^*$  = entropy of activation,

$\Delta H^*$  = enthalpy of activation,

and  $R$  = gas constant,  $8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ .

Equating the derivatives  $dk/dT$  of equations 7-4 and 7-5 gives the relation between  $\Delta E^*$  and  $\Delta H^*$ :

$$\Delta E^* = \Delta H^* + RT. \quad (7-6)$$

The derived  $\Delta E^*$  and  $\Delta H^*$  are averages obtained from data over a range of temperature, so an average value of  $T$  should be used in equation 7-6. At  $25^\circ \text{C}$  ( $77^\circ \text{F}$ ,  $298.15 \text{ K}$ ),  $RT$  is  $2.5 \text{ kJ} \cdot \text{mol}^{-1}$ . For fitting experimental data, equation 7-5 is put in logarithmic form:

$$\ln(k/T) = \ln(k'/h) + (\Delta S^*/R) - (\Delta H^*/R)(1/T). \quad (7-7)$$

The independent variable is  $1/T$ , the dependent variable is  $\ln(k/T)$ ,  $\ln(k'/h)$  and  $R$  are the constants defined above, and  $\Delta H^*$  and  $\Delta S^*$  are determined during data fitting.

The dependence of reaction rates on temperature is addressed further in chapter 12, where an equation that is more suitable for practical computations is presented and applied to an example.

## Classification of Types of Reactions

A variety of chemical reactions are discussed in this publication, and some terminology to distinguish or classify them is appropriate. The first distinction is whether changes in oxidation state occur in a reaction. Reactions in which oxidation-state changes occur are termed "redox" reactions. Beyond that distinction, further classification is useful, as outlined below with examples:

- Addition or combination reaction,  $X + Y \rightarrow Z$ . An example is  $\text{HCN} + \text{H}_2\text{O} \rightarrow \text{H-CO-NH}_2$ . This is an example of a hydration reaction, i.e., addition of  $\text{H}_2\text{O}$ . In this example,  $\text{H}_2\text{O}$  is split into  $2\text{H}^+$  and  $\text{O}^{2-}$ , which appear in the same product molecule.

- Elimination or decomposition reaction,  $Z \rightarrow X + Y$ . This is the reverse of an addition reaction. An example is  $\text{HNCS}_2^- \rightarrow \text{SCN}^- + \text{SH}^-$ .

- Condensation reaction,  $nA \rightarrow B$ . This term is applied to reactions in which the substrate molecules combine with each other. Sometimes elimination of small molecules such as  $\text{H}_2\text{O}$  occurs. Examples are  $3\text{ClCN} \rightarrow (\text{ClCN})_3$  and  $2\text{CO}(\text{NH}_2)_2 \rightarrow \text{H}_2\text{N-CO-NH-CO-NH}_2 + \text{NH}_3$ .

- Exchange or metathesis reaction,  $\text{AX} + \text{BY} \rightarrow \text{AY} + \text{BX}$ . An example is  $\text{NH}_3 + \text{HOCl} \rightarrow \text{NH}_2\text{Cl} + \text{H}_2\text{O}$ . In this reaction, e.g.,  $A$  and  $B$  are respectively  $\text{NH}_2$  and  $\text{OH}$ , and  $X$  and  $Y$  are respectively  $\text{H}$  and  $\text{Cl}$ . Another example is  $\text{H-CO-NH}_2 + \text{H}_2\text{O} \rightarrow \text{H-CO-OH} + \text{NH}_3$ . This is an example of a hydrolysis reaction. In a hydrolysis reaction,  $\text{H}_2\text{O}$  is split into  $\text{H}^+$  and  $\text{OH}^-$ , or  $2\text{H}^+$  and  $\text{O}^{2-}$ , with the  $\text{H}^+$  and  $\text{OH}^-$  or  $\text{O}^{2-}$  appearing in different molecules.

- Atom or group transfer reaction,  $A + \text{BX} \rightarrow \text{AX} + \text{B}$ . An example is  $\text{CN}^- + \text{O}_3 \rightarrow \text{NCO}^- + \text{O}_2$ , in which  $A$  is

<sup>1</sup>Italic numbers in parentheses refer to items in the list of references at the end of this chapter.



CN<sup>-</sup>, B is O<sub>2</sub>, and X is O. This class also includes hydrogen-ion transfer reactions, e.g., CN<sup>-</sup> + H<sub>2</sub>O → HCN + OH<sup>-</sup>, in which A is CN<sup>-</sup>, B is OH<sup>-</sup>, and X is H<sup>+</sup>.

- Substitution reaction, AX + Y → AY + X. An example is ClCN + SH<sup>-</sup> → SCN<sup>-</sup> + Cl<sup>-</sup> + H<sup>+</sup>, in which A is CN<sup>+</sup>, X is Cl<sup>-</sup>, and Y is S<sup>2-</sup>.

- Redistribution reaction. A redistribution reaction is an exchange reaction in which atoms or groups bound to a single atom are exchanged. An example is 2HCOS<sup>-</sup> → HCS<sub>2</sub><sup>-</sup> + HCO<sub>2</sub><sup>-</sup>.

- Disproportionation or dismutation reaction. This is a redox reaction in which a species with an element initially in one oxidation state is converted to species with that element in two different oxidation states. An example is NC-CN + 2OH<sup>-</sup> → CN<sup>-</sup> + NCO<sup>-</sup> + H<sub>2</sub>O. In this reaction, a species with carbon in the 3+ oxidation state disproportionates into species with carbon in the 2+ and 4+ oxidation states.

- Conproportionation reaction. This is the opposite of a disproportionation reaction. An example is 2H<sub>2</sub>S + SO<sub>2</sub> → 3S + 2H<sub>2</sub>O. In this reaction, the reactants contain sulfur in the 2- and 4+ oxidation states, and the product contains sulfur all in the zero oxidation state.

This classification is employed in the rest of this chapter, as described in the next section.

## Data Organization and Presentation

### Data Organization

The following sections describe the reactions of free CN<sup>-</sup> and derived species. Oxidation of CN<sup>-</sup> by different oxidants is described first. These reactions produce NCO<sup>-</sup>, ClCN (cyanogen chloride), NC-CN (cyanogen), and SCN<sup>-</sup> (thiocyanate). Then the reactions of SCN<sup>-</sup> and NCO<sup>-</sup> with oxidants are described.

In subsequent sections, the addition, exchange, and substitution reactions of free CN<sup>-</sup> and derived species are described. The names, structural chemical formulas, and the abbreviated formulas used in this chapter for the derived species are compiled in chapter 2. The derived species are classified first by carbon oxidation state, respectively 2+, 3+, and 4+, that is, C(II), C(III), and C(IV). For each of the three carbon oxidation states, the reactions are classified as follows: (1) addition or substitution reactions with H<sub>2</sub>O, NH<sub>3</sub>, and H<sub>2</sub>S/SH<sup>-</sup> (hydrogen sulfide); (2) exchange reactions, in which nitrogen- and sulfur-containing species react with NH<sub>3</sub> or H<sub>2</sub>S/SH<sup>-</sup> or undergo redistribution reactions; and (3) hydrolysis reactions of the species formed in the addition and exchange reactions.

For C(II), the initial species is CN<sup>-</sup>/HCN, {HCN}. Cyanide undergoes addition reactions with H<sub>2</sub>O, NH<sub>3</sub>, and H<sub>2</sub>S/SH<sup>-</sup>. Exchange reactions may also occur among the products of the addition reactions. The products of these

reactions undergo hydrolysis, and the ultimate product is formate (HCO<sub>2</sub><sup>-</sup>, {HCOO<sup>-</sup>}).

For C(III), the initial species is NC-CN, {NCCN}. Cyanogen undergoes addition reactions with H<sub>2</sub>O, NH<sub>3</sub>, and H<sub>2</sub>S/SH<sup>-</sup>. Exchange reactions may also occur among the products of the addition reactions. The products of these reactions undergo hydrolysis or disproportionation. The ultimate product of hydrolysis is oxalate (C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, {OOCOO<sup>-</sup>}). Disproportionation results in formation of CN<sup>-</sup> and a C(IV) species.

For C(IV), the initial species is ClCN or NCO<sup>-</sup>. Cyanogen chloride undergoes substitution reactions with H<sub>2</sub>O, NH<sub>3</sub>, or H<sub>2</sub>S/SH<sup>-</sup> to form NCO<sup>-</sup>, NCNH<sub>2</sub>, (cyanamide), and SCN<sup>-</sup>, respectively. Further addition and exchange reactions may occur, followed by hydrolysis reactions. The ultimate product is carbonate (CO<sub>3</sub><sup>2-</sup>, [COOO]).

Data are incomplete or unavailable for many of the species of interest in this publication. Where possible, inferences are made from better known reactions of organic analogs. In chemical formulas of organic species so mentioned, R represents an alkyl group.

The number of reactions in the classification outlined above is large. In the following section, all of the addition and substitution reactions are systematized, and the reactions likely to be most important in practice are indicated.

### Data Presentation

Rate data are compiled in tables in appendix F for reactions with sufficient data to generate pH and temperature profiles. In appendix F, the rate equations are in the form

$$- [Z]^{-1} [R]^{-1} d[Z]/dt = \sum_i k_i [f(\text{pH})]_i \quad (7-8)$$

$$= k(\text{pH}) \quad (7-9)$$

where  $k_i$  = rate constant,

and  $[f(\text{pH})]_i$  = pH-dependent factor.

Equation 7-8 is derived from equations 7-1, 7-2, or 7-3 by division by  $[Z]$ ,  $[Z][R]$ , or  $[Z]^2$ , respectively, and introducing the pH dependence of  $k$ . The summation term is defined in equation 7-9 as  $k(\text{pH})$ , which may be plotted versus pH to give a rate-pH profile. For reactions that are only first order in  $Z$ , the  $[R]$  term is omitted from equation 7-8. In that case, the pH-dependent half-life of  $Z$  is

$$t_{0.50} = 0.693 / k(\text{pH}). \quad (7-10)$$



For the reactions with water, described below, the substrate half-lives  $t_{0.50}$  are given for pH 11.0, which is a typical pH value in cyanide process solutions. Reactions for which sufficient data exist are illustrated with rate-pH profiles, and the pertinent tables in appendix F are cited.

### OXIDATION REACTIONS

Free  $\text{CN}^-$  and  $\text{SCN}^-$  are oxidizable by many oxidants, such as hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), ozone ( $\text{O}_3$ ), hypochlorite ( $\text{ClO}^-$ ), or peroxomonosulfate ( $\text{HSO}_5^-$ ). Peroxomonosulfate is the presumed intermediate in the  $\text{SO}_2$ -air process. Sulfur species such as elemental sulfur, polysulfides, and thiosulfate ( $\text{S}_2\text{O}_3^{2-}$ ) oxidize  $\text{CN}^-$  to  $\text{SCN}^-$ . Strong oxidants such as  $\text{O}_3$  or  $\text{ClO}^-$  also oxidize species such as  $\text{NCO}^-$ , in which the bound nitrogen is oxidized, e.g., to  $\text{N}_2$ . The following paragraphs describe the reactions of free  $\text{CN}^-$ ,  $\text{SCN}^-$ , and  $\text{NCO}^-$  with different oxidants. The oxidation reactions are schematized in figure 7-1. Figure 7-2 provides a comparison of the reduction potentials of different oxidants. The reduction potentials were calculated from the Gibbs energy data in appendix C. The oxidation reactions and their standard Gibbs energy changes are compiled in tables 7-1 and 7-2.

The oxidation of metal cyanide species by different oxidants is discussed in chapter 8.

#### Oxidation of Cyanide to Cyanate

Oxidation of  $\text{CN}^-$  to  $\text{NCO}^-$  occurs in basic solution with many oxidants, in particular those oxidants of interest for cyanide destruction. Those oxidants include  $\text{H}_2\text{O}_2$ ,  $\text{O}_3$ ,  $\text{HSO}_5^-/\text{SO}_5^{2-}$ , and  $\text{ClO}^-/\text{HClO}$ . In oxidation by  $\text{ClO}^-/\text{HClO}$ ,  $\text{ClCN}$  is formed, which hydrolyzes to  $\text{NCO}^-$ . There is evidence that oxidation of  $\text{CN}^-$  to  $\text{NCO}^-$  by  $\text{O}_2$  occurs, especially in the presence of certain catalysts.

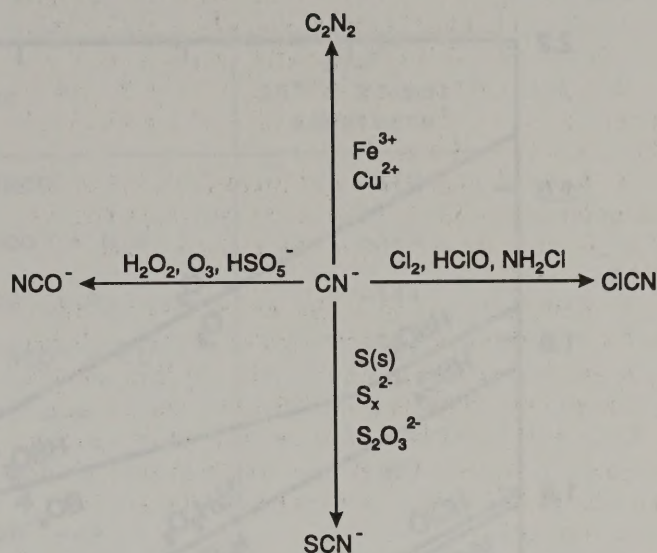
#### Hydrogen Peroxide

The uncatalyzed oxidation of  $\text{CN}^-$  by  $\text{H}_2\text{O}_2$  is reported to be very slow, but no kinetic data were located. A simultaneous reaction of  $\text{CN}^-$  with  $\text{H}_2\text{O}_2$  and  $\text{S}_2\text{O}_3^{2-}$  proceeds at an observable rate, to yield  $\text{SCN}^-$  and  $\text{SO}_4^{2-}$  (5). Hydrogen peroxide oxidation of  $\text{CN}^-$  is catalyzed by trace metals, e.g., copper or iron, such that its rate makes this reaction industrially feasible (6-7).

#### Ozone

There is much literature on the  $\text{CN}^-$ - $\text{O}_3$  reaction (8-13). In practice, the rate of this reaction is limited by mass transfer of  $\text{O}_3$  from the gas phase to the solution (8-9). Techniques for the study of fast reactions were employed primarily by Gurol and others (10-13) to study the rate and mechanism. The deduced rate law was

Figure 7-1



#### Oxidation of free cyanide.

$$d[\text{Z}]/dt = -k[\text{Z}]K_a(K_a + [\text{H}^+])^{-1}[\text{O}_3],$$

where  $[\text{Z}] = [\text{CN}^-] + [\text{HCN}]$ ,

and  $K_a$  = acidity constant of  $\text{HCN}$ , about  $10^{-9}M$ .

The rate constant  $k$  is on the order of  $10^5 M^{-1} \cdot s^{-1}$  at 200 to 25° C. Molecular  $\text{HCN}$  reacts much more slowly than  $\text{CN}^-$  with  $\text{O}_3$ . In alkaline solution, catalysis of  $\text{O}_3$  decomposition by  $\text{OH}^-$  competes with reaction with  $\text{CN}^-$ . The  $\text{CN}^-$ - $\text{O}_3$  reaction is catalyzed by copper species (11-13).

#### Peroxomonosulfate: The Sulfur Dioxide and Air Process

Oxidation of  $\text{CN}^-$  by  $\text{O}_2$  in the presence of  $\text{SO}_2$  is in use industrially as the INCO  $\text{SO}_2$ -air process (14-15). It is thought that  $\text{SO}_2$  and  $\text{O}_2$  in the alkaline slurry first react to form a peroxo species, probably  $\text{HOOSO}_3^-$ , which oxidizes  $\text{CN}^-$ . The literature search revealed no published kinetics studies.

#### Oxygen

The oxidation of  $\text{CN}^-$  by  $\text{O}_2$  is observable, but no systematic kinetic study has been published. Observations by Silver (16) showed  $\text{CO}_3^{2-}$  buildup in air-exposed  $\text{KCN}$  solutions. He made observations at 30° and 70° C on the decomposition of  $\text{KCN}$  solutions in the absence or presence of air and light. His results indicated accelerated oxidation in the presence of light. The rate increased with



Figure 7-2

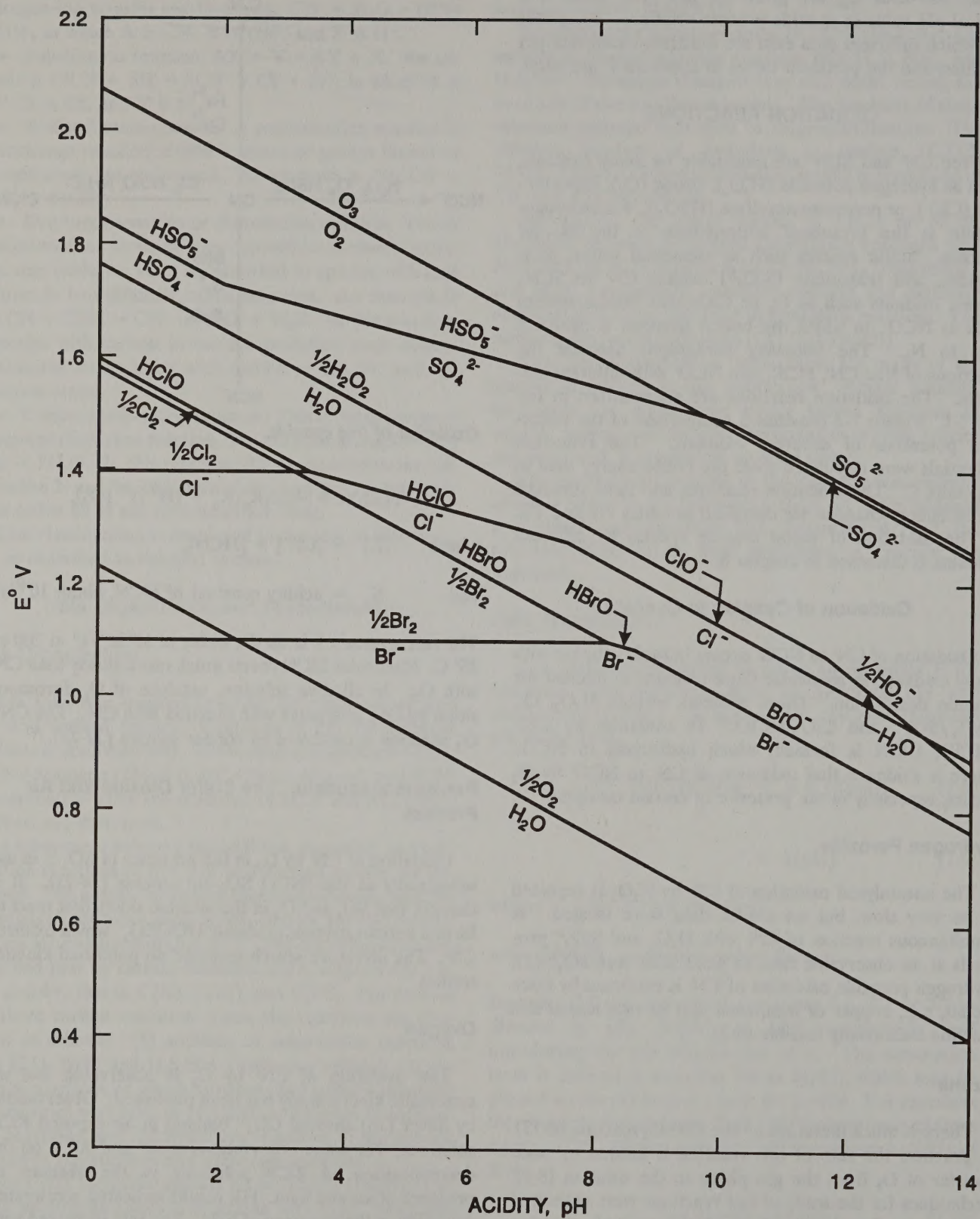
*Eh-pH diagrams for oxidants.*



Table 7-1.-Oxidation reactions of free cyanide and derived species

Substrate	Oxidant	Reaction	$\Delta_r G^\circ$ , 25° C kJ·mol <sup>-1</sup> substrate <sup>1</sup>
CN <sup>-</sup>	O <sub>2</sub>	2CN <sup>-</sup> + O <sub>2</sub> --> 2NCO <sup>-</sup>	-270
	H <sub>2</sub> O <sub>2</sub>	CN <sup>-</sup> + H <sub>2</sub> O <sub>2</sub> --> NCO <sup>-</sup> + H <sub>2</sub> O	-373
	O <sub>3</sub>	CN <sup>-</sup> + O <sub>3</sub> --> NCO <sup>-</sup> + O <sub>2</sub>	-444
	ClO <sup>-</sup>	CN <sup>-</sup> + ClO <sup>-</sup> --> NCO <sup>-</sup> + Cl <sup>-</sup>	-364
SCN <sup>-</sup>	O <sub>2</sub>	SCN <sup>-</sup> + 2O <sub>2</sub> + 2OH <sup>-</sup> --> NCO <sup>-</sup> + SO <sub>4</sub> <sup>2-</sup> + H <sub>2</sub> O	-857
	H <sub>2</sub> O <sub>2</sub>	SCN <sup>-</sup> + 4H <sub>2</sub> O <sub>2</sub> + 2OH <sup>-</sup> --> NCO <sup>-</sup> + SO <sub>4</sub> <sup>2-</sup> + 5H <sub>2</sub> O	-1,270
	O <sub>3</sub>	SCN <sup>-</sup> + 4O <sub>3</sub> + 2OH <sup>-</sup> --> NCO <sup>-</sup> + SO <sub>4</sub> <sup>2-</sup> + 4O <sub>2</sub> + H <sub>2</sub> O	-1,553
	ClO <sup>-</sup>	SCN <sup>-</sup> + 4ClO <sup>-</sup> + 2OH <sup>-</sup> --> NCO <sup>-</sup> + SO <sub>4</sub> <sup>2-</sup> + 4Cl <sup>-</sup> + H <sub>2</sub> O	-1,235
NCO <sup>-</sup>	O <sub>3</sub>	2NCO <sup>-</sup> + 3O <sub>3</sub> + OH <sup>-</sup> --> 2CO <sub>3</sub> <sup>2-</sup> + N <sub>2</sub> + 3O <sub>2</sub> + H <sub>2</sub> O	-653
	ClO <sup>-</sup>	2NCO <sup>-</sup> + 3ClO <sup>-</sup> + 2OH <sup>-</sup> --> 2CO <sub>3</sub> <sup>2-</sup> + N <sub>2</sub> + 3Cl <sup>-</sup> + H <sub>2</sub> O	-533

<sup>1</sup>Calculated from data in tables B-1 and C-1.

Table 7-2.-Conversion of free cyanide to thiocyanate

Reaction	$\Delta_r G^\circ$ , 25° C kJ·mol <sup>-1</sup> CN <sup>-</sup>
CN <sup>-</sup> + (1/8)S <sub>8</sub> (s) --> SCN <sup>-</sup>	-80
CN <sup>-</sup> + S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> --> SCN <sup>-</sup> + SO <sub>3</sub> <sup>2-</sup>	-43
CN <sup>-</sup> + S <sub>x</sub> <sup>2-</sup> --> SCN <sup>-</sup> + S <sub>x-1</sub> <sup>2-</sup>	-76 (x = 5) -72 (x = 4) -61 (x = 3)



time at 30° C, but decreased with time at 70° C. Apparently, oxidation by O<sub>2</sub> is catalyzed by impurities, very possibly iron cyanide complexes. If it is assumed that the reaction is uncatalyzed and of second order, the oxidation rate law is

$$r = k[p(\text{O}_2)][\text{CN}^-],$$

where  $p(\text{O}_2)$  = ambient O<sub>2</sub> partial pressure,

and  $k < 10^{-2} (\text{mol} \cdot \text{L}^{-1})^{-1} \cdot \text{Pa}^{-1} \cdot \text{s}^{-1}$  at 30° C.

Oxidation of CN<sup>-</sup> by O<sub>2</sub> has been reported to be catalyzed by activated carbon (17-18). In a representative experiment at pH 10.2 with 0.008M NaCN containing 25 g·L<sup>-1</sup> of activated carbon, during 48 h at 20° C, about 40 pct of the CN<sup>-</sup> was lost by oxidation to NCO<sup>-</sup>. In the absence of activated carbon, the loss of CN<sup>-</sup> was about 5 pct, attributed to volatilization of HCN. Assuming that the loss of CN<sup>-</sup> as NCO<sup>-</sup> was due to oxidation by atmospheric O<sub>2</sub>, and that the rate law is

$$r = k'[p(\text{O}_2)][\text{CN}^-][\text{C}],$$

a value of  $6 \times 10^{-7} (\text{mol} \cdot \text{L}^{-1})^{-1} \cdot \text{Pa}^{-1} (\text{g} \cdot \text{L}^{-1} \text{C})^{-1} \cdot \text{s}^{-1}$  is obtained for the rate constant  $k'$  at 20° C.

Copper has been reported to catalyze the oxidation of CN<sup>-</sup> by O<sub>2</sub> on activated carbon (19).

### Hypochlorite

The reaction of CN<sup>-</sup> with ClO<sup>-</sup>/HClO to form ClCN is very fast and is substantially complete in the time required to mix the reactants (20). The ClCN formed is subsequently hydrolyzed to NCO<sup>-</sup> (see below). This reaction is widely used for cyanide removal (21), and there is abundant literature on its industrial use. Gerritsen and Margerum (22) recently studied the reaction by spectrophotometric observation of ClO<sup>-</sup> consumption using rapid-reaction techniques at 25° C and ionic strength 1.0M. The derived rate law was

$$\begin{aligned} d[\text{CN}^-]/dt &= d[\text{ClO}^-]/dt \\ &= -(k_1 + k_2[\text{OH}^-])[\text{CN}^-][\text{ClO}^-], \end{aligned}$$

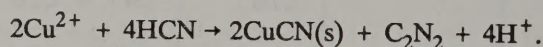
where  $k_1 = 310 \text{M}^{-1} \cdot \text{s}^{-1}$

and  $k_2 = 583 \text{s}^{-1}$ .

From these data the half-life of free CN<sup>-</sup> is calculated as 2.2 s in the presence of  $1 \times 10^{-3} \text{M}$  excess ClO<sup>-</sup> at pH 11. This result agrees with the rapid rate observed in practice. An earlier investigation of this reaction (23) gave discordant results and has been criticized (22).

### Oxidation of Cyanide to Cyanogen

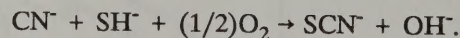
Oxidation of CN<sup>-</sup> to NC-CN occurs only in acid solutions with different oxidants. Consequently, formation of NC-CN is not expected during normal precious metals mining or closure operations, in which solutions are alkaline. However, contact of cyanide-bearing solutions with acid mine drainage or with acidic process or waste solutions could result in generation of NC-CN as well as HCN. Probably the best known instance of the formation of NC-CN is the reaction of CN<sup>-</sup>/HCN with Cu(II) species (24-25),



Oxidation of CN<sup>-</sup>/HCN to NC-CN also occurs with Fe(III) species, including [Fe(CN)<sub>6</sub>]<sup>3-</sup> (24-25). Reaction of CN<sup>-</sup>/HCN with Mn(III) or Mn(IV) oxides, MnO<sub>4</sub><sup>-</sup>, Cr(VI), or V(V) in acid solutions may yield C<sub>2</sub>N<sub>2</sub>.

### Oxidation of Cyanide to Thiocyanate

The formation of SCN<sup>-</sup> in cyanide leach solutions is attributed to the reaction of CN<sup>-</sup> with solid sulfur or dissolved S<sub>x</sub><sup>2-</sup>, or S<sub>2</sub>O<sub>3</sub><sup>2-</sup> formed by oxidation of sulfide minerals, e.g., by dissolved O<sub>2</sub>. A simplified reaction equation is



### Sulfur

The reaction of CN<sup>-</sup> with S<sub>8</sub> (the most common molecular form of sulfur) was studied in water-methanol H<sub>2</sub>O-CH<sub>3</sub>OH mixtures, 80 to 100 pct CH<sub>3</sub>OH, at 4° to 25° C (26). The reaction is first order each in CN<sup>-</sup> and S<sub>8</sub>, with a second-order rate constant of 8 to 34M<sup>-1</sup>·s<sup>-1</sup> over the reported ranges of temperature and solvent composition.

### Polysulfides

The reaction of CN<sup>-</sup> with S<sub>x</sub><sup>2-</sup> (x = 2 to 6) was studied at 25° C in 0.1M carbonate buffers and reported to be of nonintegral order (27),

$$d[\text{Z}]/dt = -k[\text{Z}]^x[\text{S}_x^{2-}]^y,$$

where  $[\text{Z}] = [\text{CN}^-] + [\text{HCN}]$ .

The values of x and y varied from 1.34 and 0.85, respectively, at pH 8.2, to 0.49 and 0.78, respectively, at pH 12.0. The value of k ranged from 0.0025M<sup>-1</sup>·s<sup>-1</sup> at pH 8.2 to 0.014M<sup>-1</sup>·s<sup>-1</sup> at pH 12.0. This study was a statistical investigation rather than a systematic effort to determine precisely the rate-limiting elementary steps and mechanism



as a function of solution composition. At initial concentrations of 0.01M each of  $\text{CN}^-$  and S as polysulfide, 50 pct of the  $\text{CN}^-$  would be converted to  $\text{SCN}^-$  in several hours and 99 pct in a few weeks at 25° C.

### Thiosulfate

The reaction of  $\text{CN}^-$  with  $\text{S}_2\text{O}_3^{2-}$  is first order in each reactant (28). At zero ionic strength, the second-order rate constant varies from  $1.2 \times 10^{-5} \text{M}^{-1} \cdot \text{s}^{-1}$  at 25° C to  $3.6 \times 10^{-4} \text{M}^{-1} \cdot \text{s}^{-1}$  at 90° C. The rate constants are 2 to 3 times higher at ionic strength 0.1 M. Data for the  $\text{CN}^-/\text{S}_2\text{O}_3^{2-}$  reaction are given in table F-1 and figure 7-3. The reaction was reported to be strongly catalyzed by copper compounds, but no data were published. At initial concentrations of 0.01M each of  $\text{CN}^-$  and  $\text{S}_2\text{O}_3^{2-}$ , 50 pct of the  $\text{CN}^-$  would be converted to  $\text{SCN}^-$  in about 3 months and 99 pct in about 30 years at 25° C and zero ionic strength. This reaction is treated as an example in chapter 12.

### Oxidation of Thiocyanate

As a rule, the oxidants that oxidize  $\text{CN}^-$  to  $\text{NCO}^-$  also oxidize  $\text{SCN}^-$ . As described below, oxidation of  $\text{SCN}^-$  usually results first in conversion to  $\text{SO}_4^{2-}$  and  $\text{CN}^-/\text{HCN}$ . The  $\text{CN}^-/\text{HCN}$  is then oxidized by more of the oxidant.

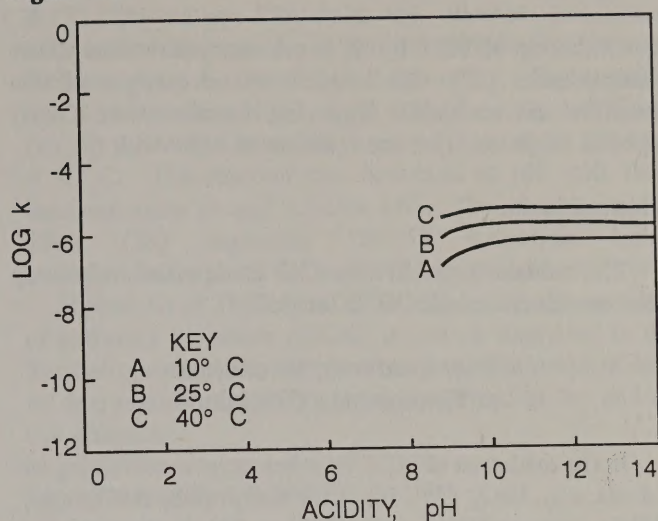
### Hydrogen Peroxide

Oxidation of  $\text{SCN}^-$  by  $\text{H}_2\text{O}_2$  was studied by Wilson and Harris (29-30). The data are presented in table F-2 and figure 7-4. At pH 4 to 11, the products are  $\text{SO}_4^{2-}$  and  $\text{NCO}^-$ ; the rate law is first order each in  $\text{SCN}^-$  and  $\text{H}_2\text{O}_2$ . At pH above 11, the rate decreases markedly; this is attributed to deprotonation of  $\text{H}_2\text{O}_2$  to  $\text{HO}_2^-$ . At pH below 2, the products are  $\text{HSO}_4^{2-}$  and  $\text{HCN}$ , and  $\text{HCN}$  has an inhibitory effect on the rate. The initial rate is first order each in  $\text{SCN}^-$ ,  $\text{H}_2\text{O}_2$ , and  $\text{H}^+$ . The kinetic complications in acid solution involve formation of  $\text{S}(\text{CN})_2$ , which undergoes further reactions (31-32). The  $\text{SCN}^-/\text{H}_2\text{O}_2$  reaction is catalyzed by copper and possibly by iron (29-30, 33). The first step in  $\text{SCN}^-$  oxidation by  $\text{H}_2\text{O}_2$  is the formation of "hypothiocyanite,"  $\text{OSCN}^-$ , which has been characterized by ultraviolet spectroscopy; the acid  $\text{HOSCN}$  has a  $\text{pK}_a$  of about 5 (34).

### Ozone

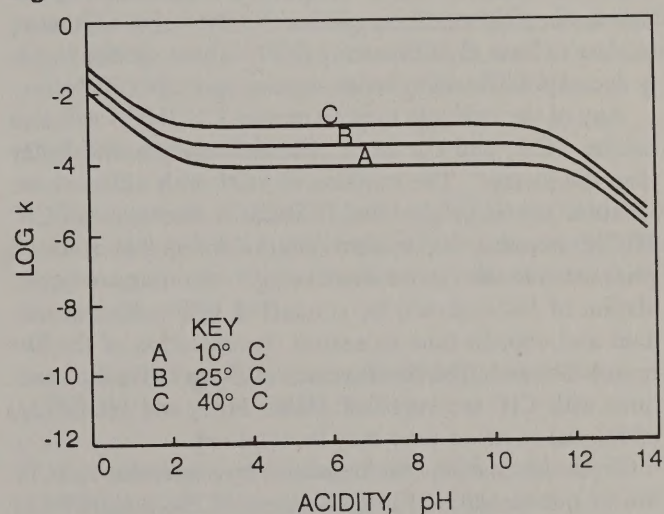
Thiocyanate is oxidized by  $\text{O}_3$  very rapidly, at a rate limited by mass transfer of  $\text{O}_3$  from gas phase to solution (35). This reaction appears to be faster than the  $\text{CN}^-/\text{O}_3$  reaction, judging by reported detection of  $\text{CN}^-$  as an intermediate. No rate constants were reported for this

Figure 7-3



Log rate constant ( $\log k$ ) versus pH for reaction of cyanide with thiosulfate.

Figure 7-4



Log  $k$  versus pH for reaction of thiocyanate with hydrogen peroxide.

reaction. For the assumed second-order reaction, the rate constant has been estimated as on the order of  $10^6 (\text{mol} \cdot \text{L}^{-1})^{-1} \cdot \text{s}^{-1}$  at ambient temperatures (35).

### Peroxomonosulfate

No information was located on the oxidation of  $\text{SCN}^-$  by  $\text{HOOSO}_3^-$ . The rate of this reaction may be comparable to the rate of oxidation of  $\text{SCN}^-$  by  $\text{H}_2\text{O}_2$ .



## Oxygen

Oxidation of  $\text{SCN}^-$  by  $\text{O}_2$  is extremely slow at ambient temperatures (29). No information on catalysis of this reaction and no kinetic data were found. Some  $\text{Cu(II)}$  species might catalyze the reaction of  $\text{SCN}^-$  with  $\text{O}_2$ .

## Hypochlorite

The oxidation of  $\text{SCN}^-$  by  $\text{ClO}^-$  is expected to be very fast; no kinetic studies were located.

### Other Oxidants; Mechanism of Thiocyanate Oxidations

In the oxidation of  $\text{SCN}^-$  by other oxygen-containing oxidants, e.g.,  $\text{BrO}_3^-$  (36),  $\text{IO}_3^-$  (37),  $\text{S}_2\text{O}_8^{2-}$  (38),  $\text{HSO}_5^-$  (39),  $\text{HNO}_2$  (40), or  $\text{HNO}_3$  (40),  $\text{HCN}$  or  $\text{CN}^-$  is observed as a product or indicated as an intermediate. Cyanide formation also occurs in the oxidation of  $\text{SCN}^-$  by  $\text{H}_2\text{O}_2$  (29-30) or  $\text{O}_3$  (35), and may occur in oxidation by  $\text{HSO}_5^-$  or  $\text{ClO}^-$ . All of the data are consistent with attack of the oxidant on the sulfur atom of  $\text{SCN}^-$ . In proposed mechanisms, the first-formed intermediate species  $\text{OSCN}^-$  reacts with more oxidant to form  $\text{O}_2\text{SCN}^-$  and  $\text{O}_3\text{SCN}^-$ . These species rapidly decompose to sulfur oxide species and  $\text{CN}^-/\text{HCN}$ .

Any of the oxidants used to oxidize  $\text{CN}^-/\text{HCN}$  will also oxidize  $\text{SCN}^-$ , and the latter reaction may proceed faster than the former. The reaction of  $\text{SCN}^-$  with different oxidants is known or expected to result in liberation of  $\text{CN}^-/\text{HCN}$ , because the oxidant attacks the sulfur atom in preference to the carbon atom in  $\text{SCN}^-$ . Consequently, oxidation of  $\text{SCN}^-$  should be conducted with sufficient oxidant and enough time to ensure the oxidation of the liberated  $\text{CN}^-$  or  $\text{HCN}$ . In the cases of  $\text{O}_3$  or  $\text{ClO}^-$ , the reactions with  $\text{CN}^-$  are very fast. With  $\text{H}_2\text{O}_2$  and  $\text{HOOSO}_3^-$ , additional reaction time may be required.

Proposals to treat cyanide wastes by conversion to  $\text{SCN}^-$  are of questionable efficacy because of the possibility of liberation of  $\text{CN}^-/\text{HCN}$  in the oxidation of  $\text{SCN}^-$  in the environment.

### Oxidation of Cyanate

Strong oxidants oxidize  $\text{NCO}^-$  to other products, generally reported or assumed to be  $\text{CO}_3^{2-}$  and  $\text{N}_2$ . As described below, the actual reaction is not always that simple.

## Ozone

Cyanate is oxidized by  $\text{O}_3$  to  $\text{CO}_3^{2-}$ ,  $\text{N}_2$ , and  $\text{NO}_3^-$ . Assuming second-order kinetics, the rate constant at 20° C is

estimated to be of the order of  $10^3 \text{M}^{-1} \cdot \text{s}^{-1}$ , which is much slower than the  $\text{CN}^-$ - $\text{O}_3$  reaction (35). In practice, the reaction rate is limited by mass transfer of  $\text{O}_3$  from the gas phase to the solution. Details concerning the formation of  $\text{NO}_3^-$  in this reaction have not been reported.

## Hypochlorite

Cyanate is oxidized by  $\text{ClO}^-$  to  $\text{CO}_3^{2-}$  and  $\text{N}_2$ ; with excess  $\text{ClO}^-$ ,  $\text{NO}_3^-$  has been reported as an accessory product. Three investigations of this reaction have been published. Lister (20, 41) investigated the reaction by monitoring the concentrations of  $\text{NCO}^-$  and  $\text{ClO}^-$  at pH 13 to 14, ionic strength 2.2M, and 50° to 75° C. He reported the rate law

$$-d[\text{NCO}^-]/dt = k'[\text{NCO}^-][\text{R}][\text{OH}^-]^{-1}.$$

Extrapolation of his data to 25° C gives  $k' = 6.2 \times 10^{-8} \text{s}^{-1}$ . If the rate law is expressed in terms of hydrogen ion concentration,

$$-d[\text{NCO}^-]/dt = k[\text{NCO}^-][\text{R}][\text{H}^+],$$

where  $[\text{R}] = [\text{ClO}^-] + [\text{HClO}]$ .

By using the relationship  $k = k'/K_w$  where  $K_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$  (appendix C), one obtains  $k = 6.2 \times 10^6 \text{M}^{-2} \cdot \text{s}^{-1}$ .

Teo and Tan (42) monitored the concentrations of  $\text{NCO}^-$  and  $\text{ClO}^-/\text{HClO}$  at pH 8.6 to 10, 27° to 50° C, and unstated ionic strength. They obtained the same rate law, with  $k = 4.8 \times 10^8 \text{M}^{-2} \cdot \text{s}^{-1}$  at 25° C. This value is nearly 80 times higher than the value derived from Lister's data.

Mapstone and Thorn (23) monitored nitrogen evolution at pH 9 to 10 and 18° C. They reported the reaction as first order each in concentrations of  $\text{NCO}^-$  and  $\text{ClO}^-$ , but did not report pH dependence. Their value of  $k$ , derived assuming a mean pH of 9.5, agrees, perhaps fortuitously, within a factor of 2 with the data of Teo and Tan extrapolated to 18° C.

The disagreement among the quoted investigators is attributed to the following:

1. All of the investigators reported induction periods before the evolution of  $\text{N}_2$  occurred.
2. The reaction is not precisely stoichiometric. Most of the investigators detected formation of  $\text{NO}_3^-$ , especially when excess  $\text{ClO}^-$  was used.
3. The  $\text{ClO}^-:\text{NCO}^- = 3:2$  stoichiometry indicates a complex reaction mechanism.

Given all of these considerations, the investigators may not have all monitored the same reaction.



## Peroxomonosulfate

No data on the oxidation of  $\text{NCO}^-$  by  $\text{HSO}_5^{2-}$  were located. Thermodynamically, the oxidant strength of  $\text{HSO}_5^{2-}$  or  $\text{SO}_5^{2-}$  is comparable to  $\text{ClO}^-$  and  $\text{O}_3$ , as shown in figure 7-2. Reaction of  $\text{NCO}^-$  with  $\text{HSO}_5\text{SO}_5^{2-}$  is possible, but would be hindered by electrostatic repulsion of the reactants.

## Hydrogen Peroxide

No information on the oxidation of  $\text{NCO}^-$  by  $\text{H}_2\text{O}_2$  was located. Thermodynamically,  $\text{H}_2\text{O}_2/\text{HO}_2^-$  is as strong an oxidant as  $\text{ClO}^-$ , as shown in figure 7-2, so reaction of  $\text{NCO}^-$  with  $\text{H}_2\text{O}_2/\text{HO}_2^-$  is certainly possible.

## Possible Mechanisms for Cyanate Oxidation

Lister (41) speculated that  $\text{HClO}$  attacks  $\text{NCO}^-$  to form an intermediate such as  $\text{Cl-NH-CO}_2^-$ , followed by further rapid oxidation by  $\text{ClO}^-/\text{HClO}$ . Teo and Tan (42) proposed a  $\text{ClO}^-/\text{HClO}$ -catalyzed hydrolysis of  $\text{NCO}^-$  to  $\text{NH}_4^+$  and  $\text{CO}_3^{2-}$ , followed by reaction of  $\text{NH}_4^+/\text{NH}_3$  with  $\text{ClO}^-/\text{HClO}$ ; this mechanism disagrees with their observed rate law.

Attack of the oxidant on the nitrogen atom is also a reasonable hypothesis and may give a species that would hydrolyze to  $\text{CO}_2$  and an oxidized nitrogen species, perhaps hydroxylamine ( $\text{NH}_2\text{OH}$ ) with  $\text{O}_3$ , or monochloramine ( $\text{NH}_2\text{Cl}$ ) with  $\text{ClO}^-$ . The oxidized nitrogen species would then react with more oxidant to produce  $\text{N}_2$  or more highly oxidized species, ultimately resulting in formation of  $\text{NO}_3^-$ .

## ADDITION, EXCHANGE, AND SUBSTITUTION REACTIONS OF CARBON(II) SPECIES

Carbon(II) is represented by  $\text{CN}^-/\text{HCN}$ , i.e.,  $\{\text{HCN}\}$ , and species derived by addition, exchange, and hydrolysis reactions. These reactions are described in this section and schematized in figures 7-5 and 7-6.

### Addition Reactions

Free  $\{\text{CN}^- \}$  undergoes addition reactions that constitute the major routes for its nonoxidative removal. The addition reactions of  $\{\text{CN}^- \}$  are schematized in figure 7-5 and discussed in the following paragraphs.

### Cyanide and Water

Cyanide undergoes addition of  $\text{H}_2\text{O}$  to yield formamide,  $\{\text{HCON}\}$ , which hydrolyzes to  $\{\text{HCOO}\}$  at a faster rate (see below) (43-44). This observation agrees with the rule that amides  $\text{R-CO-NH}_2$  hydrolyze to carboxylates,  $\text{R-CO}_2^-$

faster than nitriles  $\text{R-CN}$  undergo addition of  $\text{H}_2\text{O}$  to form  $\text{R-CO-NH}_2$  (45, pp. 1004-1010; 46). Sanchez and others (44) studied the reaction of  $\{\text{HCN}\}$  with  $\text{H}_2\text{O}$ . The rate data are given in table F-3 and figure 7-7. The reaction rate is independent of pH at pH > 10, where the half-life of  $\{\text{HCN}\}$  varies from about 80 years at  $0^\circ\text{C}$  to about 120 days at  $40^\circ\text{C}$ . The reaction rate decreases at pH < 10, then increases again in acid solution (47). The observations of Silver (16) regarding  $\{\text{HCN}\}$  hydrolysis agree semiquantitatively with the results of Sanchez and others (44).

Hydrolysis of  $\{\text{HCN}\}$  to  $\{\text{HCOO}\}$  is one of a number of pathways by which  $\{\text{HCN}\}$  is lost or degraded in industrial operations or the environment. Pathways of loss or degradation of  $\{\text{HCN}\}$  are summarized at the end of this chapter.

### Cyanide and Ammonia

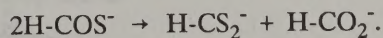
The reaction of  $\{\text{HCN}\}$  with  $\text{NH}_3$  to yield formamidine,  $\{\text{HCNN}\}$ , was observed by Oro and Kimball (43) and studied briefly by Sanchez and others (44). At  $30^\circ$  to  $60^\circ\text{C}$  and pH 7.1 to 9.6, and periods up to 14 days, no more than 0.4 pct conversion of  $\{\text{HCN}\}$  to  $\{\text{HCNN}\}$  occurred in solutions 1M in  $\text{CN}^-$  and 3M in  $\text{NH}_3$ . Hydrolysis of  $\{\text{HCNN}\}$  to  $\{\text{HCON}\}$  proceeds at a similar or faster rate, which limits the concentration of  $\{\text{HCNN}\}$ .

### Cyanide and Sulfide

The reaction of  $\{\text{HCN}\}$  with  $\text{H}_2\text{S}/\text{SH}^-$  to yield thioformamide,  $\{\text{HCSN}\}$  is known (48), but no kinetic data were located. Analogous reactions of other nitriles  $\text{R-CN}$  are known (49, p. 443).

### Exchange Reactions Involving Ammonia and Sulfide

In solutions containing both  $\text{NH}_3$  and  $\text{H}_2\text{S}/\text{SH}^-$ ,  $\{\text{HCNN}\}$ ,  $\{\text{HCSN}\}$ ,  $\{\text{HCSS}\}$ ,  $\{\text{HCON}\}$ , and  $\{\text{HCOS}\}$  may undergo exchange reactions. No information on such reactions was located, aside from an unsubstantiated statement that dithioformate,  $\{\text{HCSS}\}$ , forms via a redistribution reaction of thioformate,  $\{\text{HCOS}\}$  (50),



Exchange reactions are known for organic analogs (49, pp. 428, 443, 454; 51, pp. 719, 736, 749). They include

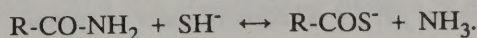
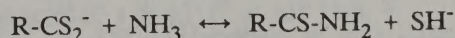
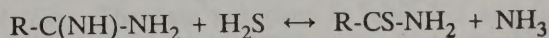
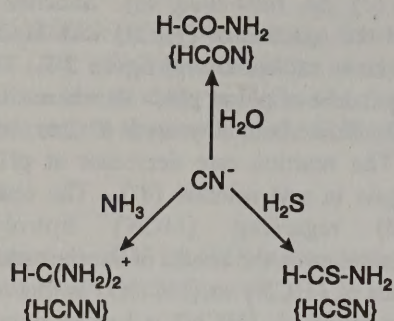


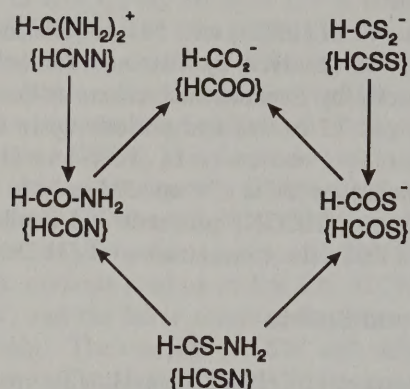


Figure 7-5



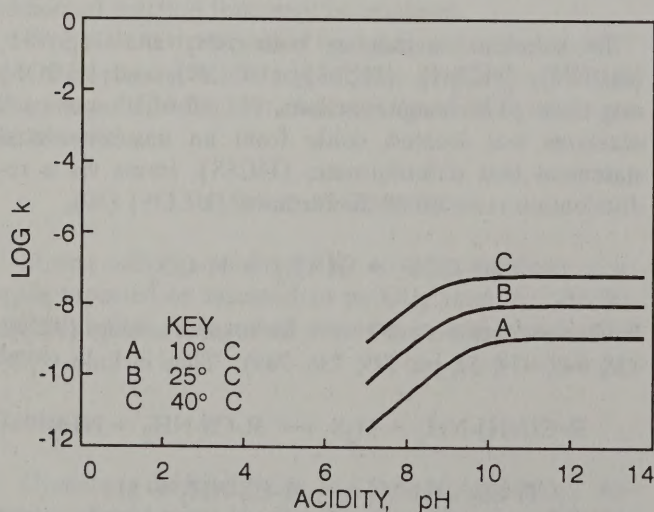
Addition reactions of free cyanide.

Figure 7-6



Hydrolysis reactions of carbon(II) species.

Figure 7-7



Log *k* versus pH for addition of water to cyanide.

The failure to observe {HCOS} in the hydrolysis of {HCSN} may have been due to the presence of NH<sub>3</sub> in the reaction solution (44). At the low concentrations of NH<sub>3</sub> and H<sub>2</sub>S/SH<sup>-</sup> in process and impounded solutions, such exchange reactions are not expected to be significant.

### Hydrolysis Reactions

The products of the addition reactions of {HCN} undergo hydrolysis and are thereby finally converted to {HCOO}. These reactions are discussed in this section and schematized in figure 7-5.

### Formamidine

The hydrolysis of {HCNN} gives {HCON}. Sanchez and others (44) report brief observations that suggest a half-life at 30° C of 7 to 14 days at pH 7.1, to 2 to 4 h at pH 9.5. As a rule, amidines R-C(NH)-NH<sub>2</sub> hydrolyze to R-CO-NH<sub>2</sub> much faster than R-CO-NH<sub>2</sub> hydrolyzes to R-CO<sub>2</sub><sup>-</sup> (45, p. 498; 46). Acetamidine (R = CH<sub>3</sub>) hydrolyzes to acetamide (CH<sub>3</sub>CONH<sub>2</sub>) rapidly in water at 25° C (46).

### Thioformamide

Sanchez and others (44) report that the main product of hydrolysis of {HCSN} is {HCON}; formation of {HCOS} was not observed. Their brief observations indicate a half-life at 30° C of 3 days at pH 8.5. For comparison, organic thioamides R-CS-NH<sub>2</sub>, e.g., thioacetamide (R = CH<sub>3</sub>), hydrolyze to both R-CO-NH<sub>2</sub> and R-COS<sup>-</sup> (49, p. 448; 52-53). The relative amounts of products depend on temperature and pH. With acetamide, hydrolysis to R-CO-NH<sub>2</sub> predominates in acid solution, and hydrolysis to R-COS<sup>-</sup> predominates in basic solution (49, pp. 448; 52-54). It is possible that {HCOS} forms in the hydrolysis of {HCSN} under other conditions than Sanchez and others (44) studied.

### Dithioformate

No information was located on the rate of hydrolysis of {HCSS}. The organic analogs R-CS<sub>2</sub><sup>-</sup> hydrolyze slowly (52, pp. 719, 732, 750). Oxidation by O<sub>2</sub> or other oxidants may compete with hydrolysis (51, pp. 723, 750). Dithioformate in solution as its alkali metal salts forms complexes with heavy metal ions, so hydrolysis is not readily catalyzed by heavy metal cations (54); contrast the behavior of {HCOS} (see below).

### Formamide

The hydrolysis of {HCON} to {HCOO} and NH<sub>3</sub> was studied at 80° C (55) and at 25° to 50° C (56-57). The



results from Salem and Sidahmed (56-57) are given in table F-4 and figure 7-8. At pH 11, the half-life of {HCON} varies from about 50 days at 0° C to about 1.5 days at 40° C. The half-life for addition of H<sub>2</sub>O to CN<sup>-</sup> is much longer than that for hydrolysis of {HCON}, being longer by factors of 600 and 80 at 0° and 40° C, respectively. Consequently, {HCON} does not accumulate during the conversion of CN<sup>-</sup> to {HCOO<sup>-</sup>}. These results parallel the trends observed for organic analogs (45, pp. 1004-1010; 46, 52). The rate constants calculated for 80° C from the data of Salem and Sidahmed (56-57) differ from those of Hine and others (55) by 3 and 30 pct, respectively, for acid and alkaline hydrolysis.

### Thioformate

No data on the hydrolysis of {HCOS} were located. Organic analogs R-COS<sup>-</sup> hydrolyze slowly in acidic or basic solutions (51, pp. 719, 732, 750; 52, 58-59); half-lives are months at 70° C at pH 2 to 10. Thioformate in solution as its alkali metal salts reacts with heavy metal cations to precipitate the metal sulfides, which indicates catalyzed hydrolysis (54). Oxidation by O<sub>2</sub> or other oxidants may compete with hydrolysis (51, pp. 723, 750), though it too is slow, as no oxidation was detected in solutions of thioacetic acid (CH<sub>3</sub>-CO-SH) in 7 days at room temperature (60).

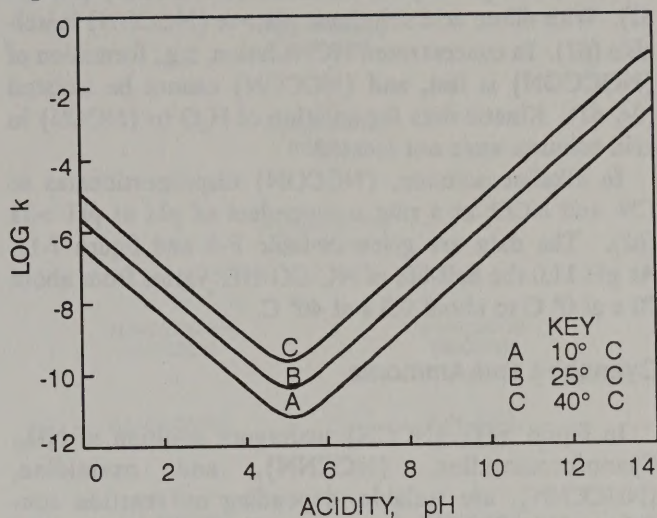
### ADDITION, EXCHANGE, AND SUBSTITUTION REACTIONS OF CARBON(III) SPECIES

Carbon(III) is represented by {NCCN} and species derived from it by addition, exchange, and hydrolysis reactions. Disproportionation reactions also occur with formation of equimolar quantities of C(II) and C(IV) species. Insofar as {NCCN} is formed by oxidation of {HCN} only in acid solutions, the species described in this section are not likely to be encountered in normal precious metals operations. Contact of cyanide solutions with acidic solutions such as acid mine drainage may result in formation of {NCCN} via oxidation by Fe(III) or Cu(II), e.g., and hence the species derived from it described below. Cyanogen is unstable at all pH values with respect to disproportionation to CN<sup>-</sup>/HCN and NCO<sup>-</sup> as shown in figure E-3.

#### Addition Reactions

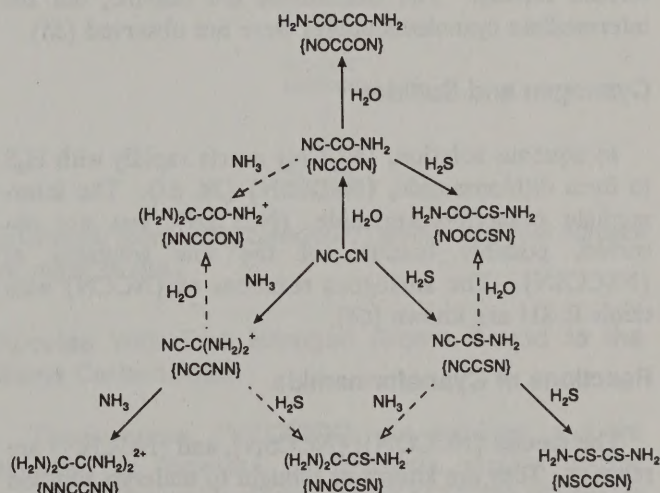
The addition reactions of {NCCN} are schematized in figure 7-9 and discussed in the following paragraphs. Since {NCCN} has two CN groups, the possible reaction products are more numerous than with {HCN}. Addition of one molecule of H<sub>2</sub>O, NH<sub>3</sub>, or H<sub>2</sub>S results in formation of species {NCCNX}, which undergo addition of a second

Figure 7-8



Log *k* versus pH for hydrolysis of formamide.

Figure 7-9



Addition reactions of cyanogen.

molecule of reagent to form {YNCCNX}, where X and Y represent oxygen, nitrogen, or sulfur.

#### Cyanogen and Water

Cyanogen disproportionates rapidly to CN<sup>-</sup> and NCO<sup>-</sup> in basic solution, in part via addition of H<sub>2</sub>O to form cyanoformamide, {NCCON} (24, 61-62). The rate was observed to vary directly with OH<sup>-</sup> concentration at pH 10 to 12 (62). The data are given in table F-5 and figure 7-10. The half-life of {NCCN} varies from about 2 s at 0° C to about 0.07 s at 40° C, at pH 11.0.

Addition of water to {NCCN} in acid solution gives {NCCON}, which in turn undergoes addition of a second



molecule of  $\text{H}_2\text{O}$  to yield oxamide,  $\{\text{NOCCON}\}$  (24, 61-62). With dilute acid solutions,  $\text{pH} > 0$ ,  $\{\text{NCCON}\}$  is isolable (61). In concentrated  $\text{HCl}$  solution, e.g., formation of  $\{\text{NOCCON}\}$  is fast, and  $\{\text{NCCON}\}$  cannot be isolated (24, 61). Kinetic data for addition of  $\text{H}_2\text{O}$  to  $\{\text{NCCN}\}$  in acid solution were not located.

In alkaline solution,  $\{\text{NCCON}\}$  disproportionates to  $\text{CN}^-$  and  $\text{NCO}^-$  at a rate independent of  $\text{pH}$  at  $\text{pH} > 11$  (62). The data are given in table F-6 and figure 7-11. At  $\text{pH} 11.0$  the half-life of  $\text{NC-CO-NH}^-$  varies from about 70 s at  $0^\circ\text{C}$  to about 0.3 s at  $40^\circ\text{C}$ .

### Cyanogen and Ammonia

In liquid  $\text{NH}_3$ ,  $\{\text{NCCN}\}$  undergoes addition of  $\text{NH}_3$ . Cyanoformamidine,  $\{\text{NCCNN}\}$ , and oxamidine,  $\{\text{NNCCNN}\}$ , are isolable, depending on reaction conditions (63-64). No data are available concerning the formation of  $\{\text{NCCNN}\}$  and  $\{\text{NNCCNN}\}$  in the reaction of  $\{\text{NCCN}\}$  with aqueous  $\text{NH}_3$ . In concentrated aqueous solutions of organic amines, the organic oxamidines are formed rapidly. The oxamidines are isolable, but the intermediate cyanoformamides were not observed (65).

### Cyanogen and Sulfides

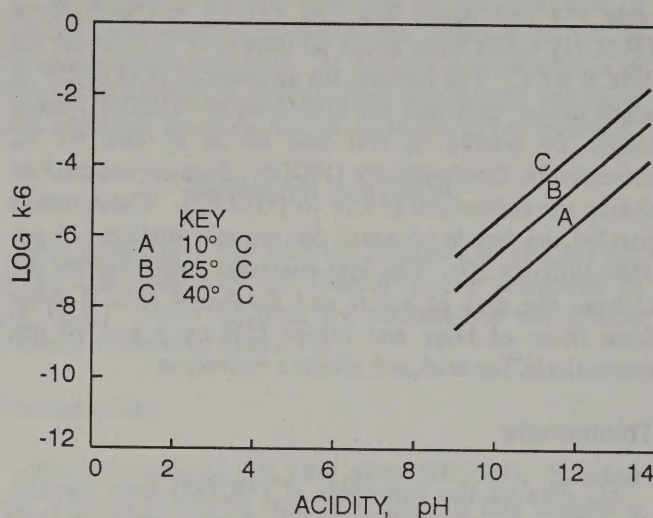
In aqueous solution,  $\{\text{NCCN}\}$  reacts rapidly with  $\text{H}_2\text{S}$  to form dithiooxamide,  $\{\text{NSCCSN}\}$  (24, 61). The intermediate cyanthioformamide,  $\{\text{NCCSN}\}$ , was not observed, possibly because of the low solubility of  $\{\text{NSCCSN}\}$ . The analogous reactions of  $\{\text{NCCN}\}$  with thiols  $\text{R-SH}$  are known (66).

### Reactions of Cyanoformamide

The species  $\{\text{NCCON}\}$ ,  $\{\text{NCCSN}\}$ , and  $\{\text{NCCNN}\}$  are reactive. They are known or thought to undergo addition or disproportionation reactions, as schematized in figure 7-12. The disproportionation of  $\{\text{NCCON}\}$  was discussed above in connection with the addition of  $\text{H}_2\text{O}$  to  $\{\text{NCCN}\}$ . Cyanoformamide undergoes addition of  $\text{H}_2\text{S}$  to form thiooxamide,  $\{\text{NSCCON}\}$  (61), and probably undergoes addition of  $\text{NH}_3$  to form amidinoformamide,  $\{\text{NNCCON}\}$ . Other possible but undemonstrated addition reactions to give  $\{\text{NNCCON}\}$ ,  $\{\text{NSCCON}\}$ , and amidinothioformamide,  $\{\text{NNCCSN}\}$ , are shown in figure 7-12.

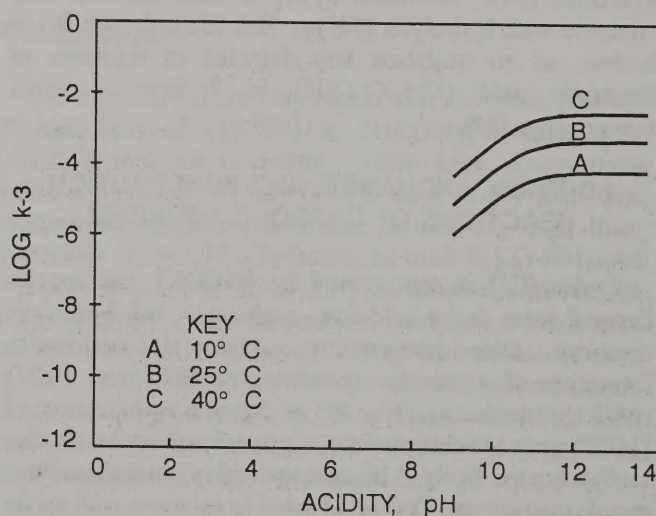
Cyanoformamide in warm water disproportionates to  $\{\text{HCN}\}$  and  $\text{HNCO}$ , which hydrolyzes to  $\text{CO}_2$  and  $\text{NH}_3$  (see below) (61). The disproportionation of  $\{\text{NCCON}\}$  in basic solution is described above. The species  $\{\text{NCCSN}\}$  and  $\{\text{NCCNN}\}$  may also disproportionate to  $\{\text{HCN}\}$  and  $\text{SCN}^-$  and cyanamide,  $\{\text{NCN}\}$ , respectively; no data were located. These reactions are also schematized in figure 7-12.

Figure 7-10



Log  $k$  versus  $\text{pH}$  for addition of water to cyanogen.

Figure 7-11



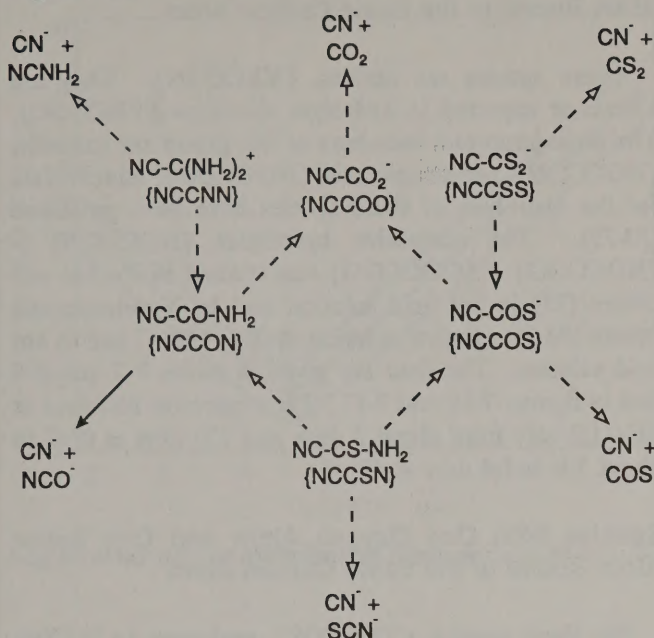
Log  $k$  versus  $\text{pH}$  for disproportionation of cyanoformamide.

### Exchange Reactions Involving Ammonia and Sulfide

In solutions containing both  $\text{NH}_3$  and  $\text{H}_2\text{S}/\text{SH}^-$ , the species formed in addition and substitution reactions of  $\{\text{NCCN}\}$  may undergo exchange reactions. No information on such reactions was located. Such exchange reactions are known for organic analogs (66-69). At the low concentrations of  $\text{NH}_3$  and  $\text{H}_2\text{S}/\text{SH}^-$  in process and impounded solutions, the extent of such reactions is expected to be negligible.



Figure 7-12



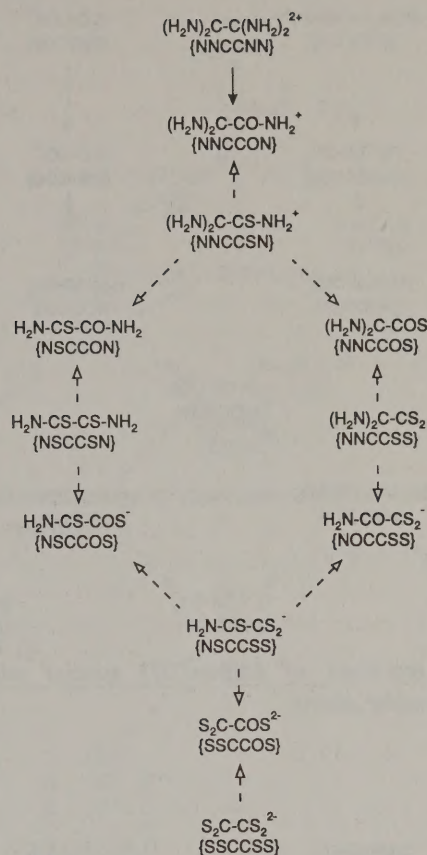
Reactions of carbon(III) species {NCCXY}.

### Hydrolysis Reactions

Hydrolysis of the species {NCCXY}, where X and Y are oxygen, nitrogen, or sulfur, to cyanoformate, {NCCOO}, has not been demonstrated. The addition and disproportionation reactions mentioned in the preceding section evidently compete with hydrolysis. Neither cyanoformic acid nor its salts {NCCOO} have ever been isolated; presumably disproportionation to {HCN} and {COOO} occurs rapidly. These reactions are schematized in figure 7-12.

The hydrolysis reactions of species formed by addition of two molecules of  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , or  $\text{H}_2\text{S}$  to one of {NCCN} are described in the remainder of this section and schematized in figures 7-13 through 7-15. The final hydrolysis product is (OCCOO). Many of these species are not expected to be important in practice, and the discussion is appropriately brief. Moreover, there are no kinetic data for most of them. In the abbreviated formulas, X and Y represent oxygen, nitrogen, or sulfur. The discussion is arranged according to the identity of the atoms bound to any one carbon atom in the substrate, namely {YXCCNN}, {YXCCSN}, etc. regardless of the identity of X and Y. The species are arranged in order of increasing number of oxygen atoms, i.e., increasing extent of hydrolysis.

Figure 7-13



Hydrolysis reactions of carbon(III) species with four nitrogen or sulfur atoms.

### Species With Two Nitrogen Atoms Bound to the Same Carbon Atom

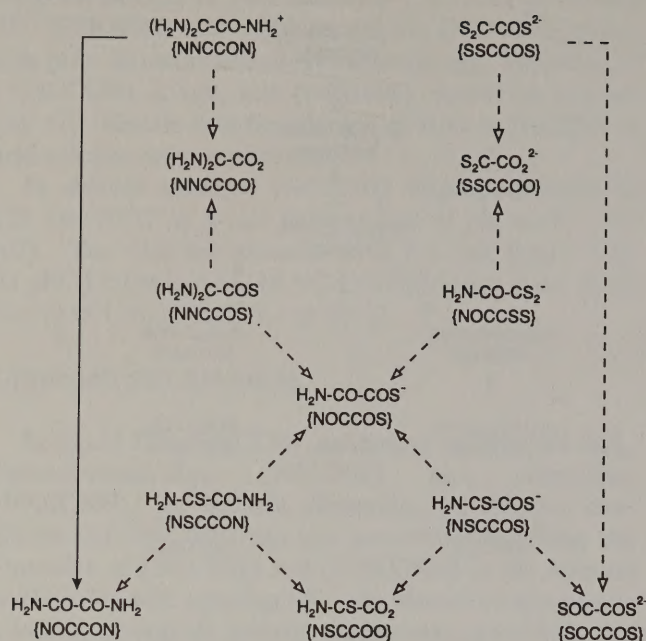
These species, {YXCCNN}, are amidines, and are reported or expected to hydrolyze rapidly to the corresponding amide derivatives {YXCCON} (68-69), as described above for {HCNN}. This is known to occur with organic analogs of {NNCCNN} (65). No kinetic data were located.

### Species With One Nitrogen Atom and One Sulfur Atom Bound to the Same Carbon Atom

These are thioamides, {YXCCSN}, and are reported or expected to hydrolyze to {YXCCON} and {YXCCOS} (69-70) by analogy with other thioamides as described above for {HCSN}. The most important species in this group is {NSCCSN}. No kinetic data were located for the hydrolysis of {NSCCSN}.

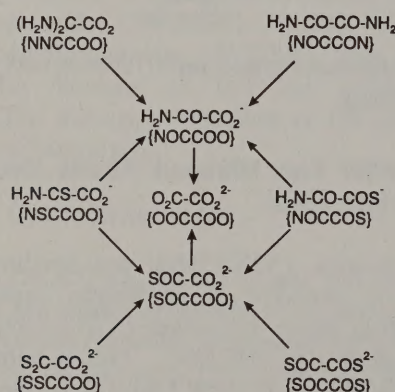


Figure 7-14



Hydrolysis reactions of carbon(III) species with three nitrogen or sulfur atoms.

Figure 7-15



Hydrolysis reactions of carbon(III) species with two nitrogen or sulfur atoms.

### Species with Two Sulfur Atoms Bound to the Same Carbon Atom

These species, {YXCCSS}, may form via redistribution reactions of {YXCCOS}. As with R-CS<sub>2</sub><sup>-</sup>, described above under hydrolysis of C(II) species, hydrolysis and oxidation are expected to compete. No kinetic data were located. The syntheses of 1,1-dithiooxalate, {OCCCSS}, trithiooxalate, {SOCCSS}, and tetrathiooxalate, {SSCCSS}, were conducted in an inert atmosphere (71-72).

### Species With One Oxygen Atom and One Nitrogen Atom Bound to the Same Carbon Atom

These species are amides, {YXCCON}. They are known or expected to hydrolyze slowly to {YXCCOO}. The most important members of this group are oxamide, {NOCCON}, and oxamic acid, {NOCCOO}. Kinetic data for the hydrolysis of these species have been published (73-75). The successive hydrolyses {NOCCON} → {NOCCOO} → {OCCOO} was studied by Packer and others (73) in hot acid solution and by Voortman and others (74-75) alkaline solution at 0° to 60° C and in hot acid solution. The data are given in tables F-7 and F-8 and in figures 7-16 and 7-17. The respective half-lives at pH 11.0 vary from about 2 days and 120 days at 0° C to about 5 h and 4 days at 40° C.

### Species With One Oxygen Atom and One Sulfur Atom Bound to the Same Carbon Atom

For these species, {YXCCOS}, analogous to R-COS<sup>-</sup> described above, hydrolysis and oxidation are expected to compete. Thiooxalate, {OCCCOS}, was prepared under an inert atmosphere (71). Fast hydrolysis at pH < 2 was reported for 1,2-dithiooxalate, {SOCCOS} (76).

### ADDITION, EXCHANGE, AND SUBSTITUTION REACTIONS OF CARBON(IV) SPECIES

Carbon(IV) is represented by ClCN and NCO<sup>-</sup> and species derived by addition, exchange, hydrolysis, and substitution reactions. The oxidation of CN<sup>-</sup> by chlorine oxidants such as ClO<sup>-</sup> gives ClCN, and oxidation by oxygen oxidants such as H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>, and HOOSO<sub>3</sub><sup>-</sup> gives NCO<sup>-</sup>. Thus ClCN and NCO<sup>-</sup> are important intermediates in the oxidative destruction of CN<sup>-</sup>, and the species derived by addition, exchange, hydrolysis, and substitution reactions are of interest.

### Reactions of Cyanogen Halides

The cyanogen halides form when {HCN} reacts with halogens or hypohalites. In cyanide destruction by hypochlorite oxidation, ClCN is the primary product. Bromine or hypobromite oxidation of {HCN} gives BrCN. The cyanogen halides undergo substitution reactions with H<sub>2</sub>O, NH<sub>3</sub>, or H<sub>2</sub>S/SH<sup>-</sup>, to form NCO<sup>-</sup>, H<sub>2</sub>NCN, and SCN<sup>-</sup>, respectively. A conceivable mechanism is addition of the reagent to cyanogen halide, followed by rapid elimination of hydrogen halide. These reactions are described in this section and schematized in figure 7-18.



Figure 7-16

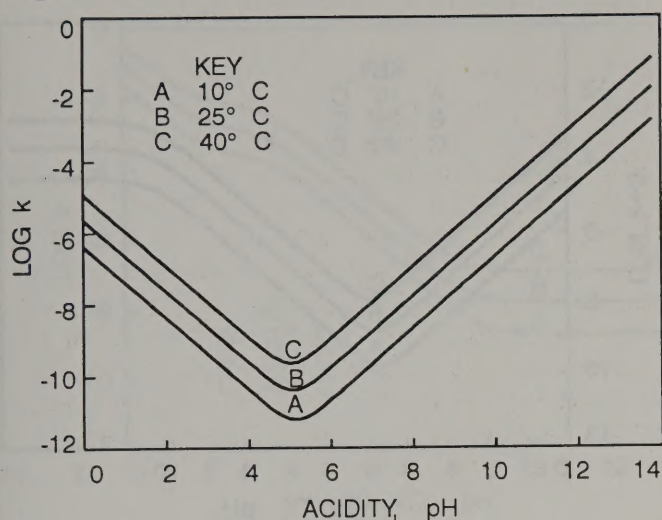
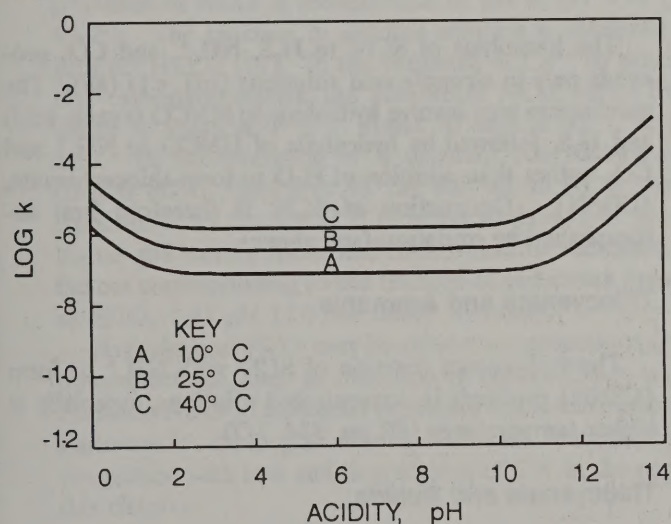
Log *k* versus pH for hydrolysis of oxamide.

Figure 7-17

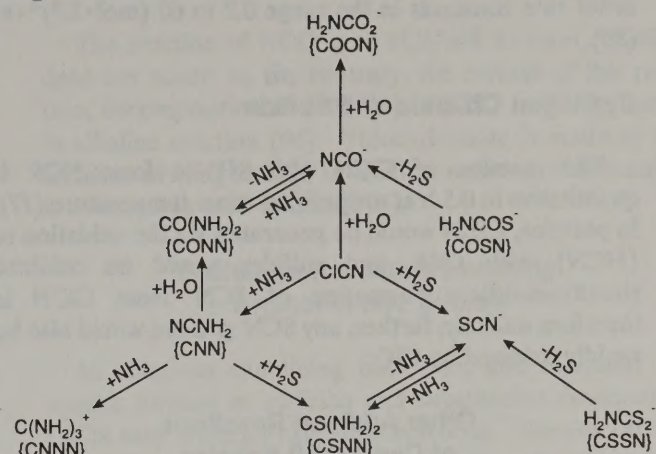
Log *k* versus pH for hydrolysis of oxamic acid.

### Cyanogen Chloride and Water

Cyanogen chloride, ClCN, hydrolyzes to NCO<sup>-</sup> in alkaline solution (77-80). The data are presented in table F-9 and figure 7-19. At pH above 6, the rate is proportional to OH<sup>-</sup> concentration. At pH 11.0, the half-life varies from about 4 h at 0° C to about 4 s at 40° C. Hydrolysis of ClCN is catalyzed by CO<sub>3</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, H<sub>2</sub>O<sub>2</sub>, Cl<sub>2</sub>, and ClO<sup>-</sup> (79-80); the data are incomplete.

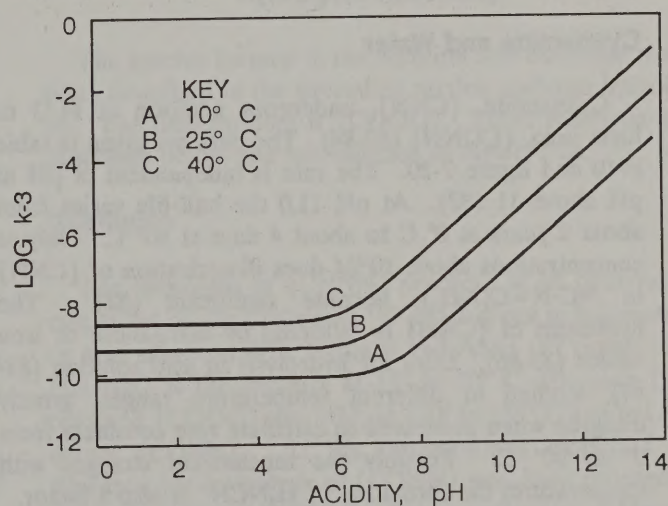
Cyanate, formed directly as an oxidation product of CN<sup>-</sup> or via hydrolysis of ClCN, is the most important intermediate in the oxidative destruction of CN<sup>-</sup>. Its hydrolysis to NH<sub>3</sub> and HCO<sub>3</sub><sup>-</sup> is described below.

Figure 7-18



Substitution reactions of cyanogen chloride and subsequent addition reactions.

Figure 7-19

Log *k* versus pH for hydrolysis of cyanogen chloride.

The hydrolysis of BrCN proceeds similarly to that of ClCN but about 1 power of 10 slower (81). The data are incomplete.

### Cyanogen Chloride and Ammonia

The reaction of ClCN with aqueous NH<sub>3</sub> to form H<sub>2</sub>NHCN was reported to be no faster than its hydrolysis to NCO<sup>-</sup> with 10<sup>-4</sup>M to 10<sup>-3</sup>M reactants at pH 8 and unspecified room temperature (77). No systematic study was located. However, a more recent study of ClCN substitution reactions with different amines, including hydroxylamine (NH<sub>2</sub>OH), hydrazine (N<sub>2</sub>H<sub>4</sub>), and methylamine (CH<sub>3</sub>NH<sub>2</sub>),



reports fast reactions at 25° C and pH 4 to 6, with second-order rate constants in the range 0.2 to 60 (mol·L<sup>-1</sup>)<sup>-1</sup>·s<sup>-1</sup> (80).

### Cyanogen Chloride and Sulfide

The reaction of ClCN with SH<sup>-</sup> to form NCS<sup>-</sup> is quantitative in 0.5 h at unspecified room temperature (77). In practice, ClCN would be generated via the oxidation of {HCN} with ClO<sup>-</sup>, and sulfides would be oxidized simultaneously. Formation of SCN<sup>-</sup> from ClCN is therefore unlikely; further, any SCN<sup>-</sup> present would also be rapidly oxidized by ClO<sup>-</sup>.

### Other Addition Reactions of Carbon(IV) Species

Figure 7-18 also shows species that would be expected to form by further addition reactions of NCO<sup>-</sup>, H<sub>2</sub>NCN, and NCS<sup>-</sup>. As shown there and described below, some of those species, on the contrary, undergo the reverse of those addition reactions.

### Cyanamide and Water

Cyanamide, {CNN}, undergoes addition of H<sub>2</sub>O to form urea, {CONN} (82-84). The data are given in table F-10 and figure 7-20. The rate is independent of pH at pH above 11 (82). At pH 11.0 the half-life varies from about 2 years at 0° C to about 4 days at 40° C. Only at concentrations above 10<sup>-2</sup>M does dimerization of {CNN} to NC-N=C(NH<sub>2</sub>)<sub>2</sub> become significant (82). The hydrolysis of {CNN} is catalyzed by manganese or iron oxides (85-86). Data for hydrolysis in acid solution (83-84), studied in different temperature ranges, grossly disagree when processed to calculate rate constants from 0° to 90° C. Possibly the mechanism changes with temperature; the formation of H<sub>3</sub>NCN<sup>+</sup> is also a factor.

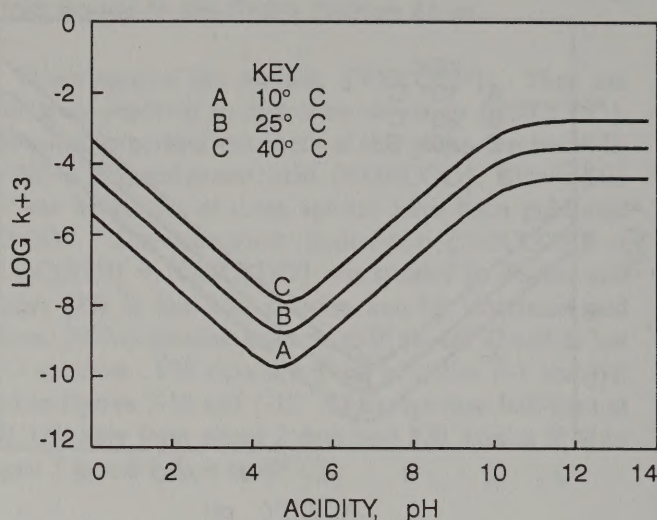
### Cyanamide and Ammonia

The reaction of {CNN} with NH<sub>3</sub> to form guanidine, {CINN}, is well known (45, pp. 1098-1099). Usually an ammonium salt is the reagent, and the guanidinium salt is the product. No kinetic data for this reaction in aqueous solution were located.

### Cyanamide and Sulfide

The reaction of {CNN} with H<sub>2</sub>S/SH<sup>-</sup> to form thiourea, {CSNN}, is well known (49, p. 456); kinetic data were also published (87).

Figure 7-20



Log *k* versus pH for addition of water to cyanamide.

### Thiocyanate and Water

The hydrolysis of SCN<sup>-</sup> to H<sub>2</sub>S, NH<sub>4</sub><sup>+</sup>, and CO<sub>2</sub> proceeds only in strongly acid solutions (pH < 1) (88). The mechanism may involve hydrolysis to HNCO (cyanic acid) and H<sub>2</sub>S, followed by hydrolysis of HNCO to NH<sub>4</sub><sup>+</sup> and CO<sub>2</sub>, rather than addition of H<sub>2</sub>O to form thiocarbamate, {COSN}. Destruction of SCN<sup>-</sup> is therefore best accomplished by oxidation (see above).

### Thiocyanate and Ammonia

The well-known reaction of SCN<sup>-</sup> with NH<sub>4</sub><sup>+</sup> to form {CSNN} proceeds in concentrated solutions, especially at higher temperatures (89, pp. 334, 342).

### Thiocyanate and Sulfide

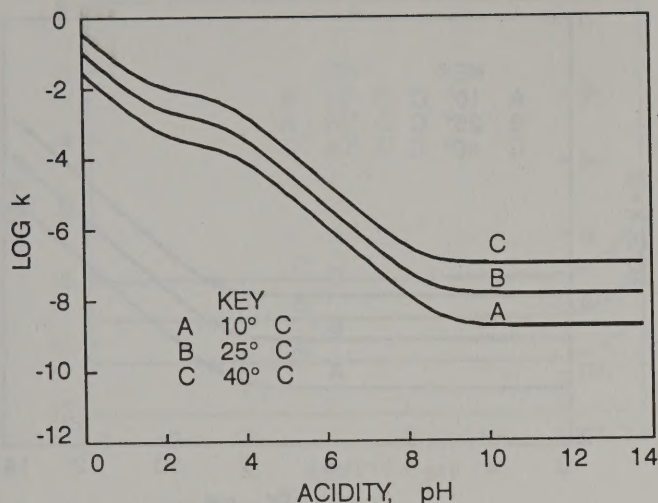
The reaction of SCN<sup>-</sup> with H<sub>2</sub>S/SH<sup>-</sup> to form dithiocarbamate, {CSSN}, does not occur; on the contrary, the reverse of this reaction, decomposition of {CSSN} to SCN<sup>-</sup> and SH<sup>-</sup>, occurs in alkaline solution (90-91). Dithiocarbamate is made by the addition of NH<sub>3</sub> to CS<sub>2</sub> in alkaline solution; this reaction is reversed in acid solution (90, 92).

### Cyanate and Water

The addition reaction of NCO<sup>-</sup> with H<sub>2</sub>O gives carbamate, {COON}, which in turn hydrolyzes much faster to NH<sub>3</sub> and {COOO} (see below). The data are given in



Figure 7-21

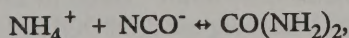
Log *k* versus pH for addition of water to cyanate.

tables F-11 and F-12 and figure 7-21. The rate of disappearance of  $\text{NCO}^-$  is independent of pH at  $\text{pH} > 10$  (20, 93-95). The reaction in alkaline solution is catalyzed by product  $\text{HCO}_3^-$  (95). In the presence of  $\text{Ca}^{2+}$  to precipitate carbonate species, the half-life of  $\text{NCO}^-$  varies from about 50 years at  $0^\circ\text{C}$  to about 70 days at  $40^\circ\text{C}$  at pH 11.0. In the presence of a constant concentration of  $0.010\text{M}$   $\text{HCO}_3^-$  (pH 8 to 9), the half-life of  $\text{NCO}^-$  varies from about 1.7 years at  $0^\circ\text{C}$  to about 14 days at  $40^\circ\text{C}$ . At higher pH values, these half-lives would be increased by factors corresponding to the fraction of carbonate present as  $\text{HCO}_3^-$ . At pH 11.0 this factor is about 5.

Hydrolysis of  $\text{NCO}^-$  may be subject to competition from other reactions, such as oxidation to  $\text{N}_2$  and  $\text{CO}_3^{2-}$ , which consume  $\text{NCO}^-$  in industrial processes or the environment. Pathways for the degradation of  $\text{NCO}^-$  are summarized in connection with loss and degradation of  $\text{CN}^-$  at the end of this chapter.

### Cyanate and Ammonia

The well-known reaction of  $\text{NCO}^-$  with  $\text{NH}_4^+$  to form  $\{\text{CONN}\}$ , proceeds in concentrated solutions, especially at higher temperatures (89, pp. 334, 342; 93). For the equilibrium of  $\{\text{CONN}\}$  with  $\text{NH}_4^+$  and  $\text{NCO}^-$ ,



log *K* is +4.7, calculated from Gibbs energy data in tables B-1 and C-1. Kinetic data for the formation of  $\{\text{CONN}\}$  from  $\text{NH}_4^+$  and  $\text{NCO}^-$  are given in table F-13 (93).

### Cyanate and Sulfide

The reaction of  $\text{NCO}^-$  with  $\text{H}_2\text{S}/\text{SH}^-$  to form  $\{\text{COSN}\}$  does not occur; on the contrary, the reverse of this reaction, decomposition of  $\{\text{COSN}\}$  to  $\text{NCO}^-$  and  $\text{SH}^-$ , occurs in alkaline solution (96). Thiocarbamate is made by the addition of  $\text{NH}_3$  to  $\text{COS}$  in alkaline solution; this reaction is reversed in acid solution (96).

### Exchange Reactions Involving Ammonia and Sulfide

In solutions containing both  $\text{NH}_3$  and  $\text{H}_2\text{S}/\text{SH}^-$ , the species formed in addition and substitution reactions of  $\text{ClCN}$  may undergo exchange reactions. Species such as  $\{\text{COSN}\}$ ,  $\{\text{CSSN}\}$ , and  $\{\text{CSSS}\}$  (trithiocarbonate) could conceivably form. As stated above for C(II) and C(III) species, such reactions are unlikely to be significant at the low concentrations of the reactants in process solutions.

### Hydrolysis Reactions

The species formed in the addition and exchange reactions described in the preceding section undergo hydrolysis. The final product is  $\{\text{COOO}\}$ . These reactions are described below and schematized in figure 7-22.

### Guanidine

The hydrolysis of  $\{\text{CNNN}\}$  proceeds at an observable rate in hot alkaline solutions (97-98), but not in hot neutral or acid solutions (97). Homer and Alwis (97) report that  $\{\text{CONN}\}$  is the product at  $15^\circ$  to  $70^\circ\text{C}$ ; Eloranta (98) obtained  $\{\text{COOO}\}$  and  $\text{NH}_3$  at  $130^\circ$  to  $135^\circ\text{C}$  and did not detect  $\{\text{CONN}\}$ . At the temperatures employed by Eloranta, the hydrolysis of  $\{\text{CONN}\}$  may have proceeded faster than that of  $\{\text{CNNN}\}$ . The investigation of Homer and Alwis appears more systematic, and includes comparison with hydrolyses of related substrates. The data are given in table F-14 and figure 7-23.

### Thiourea

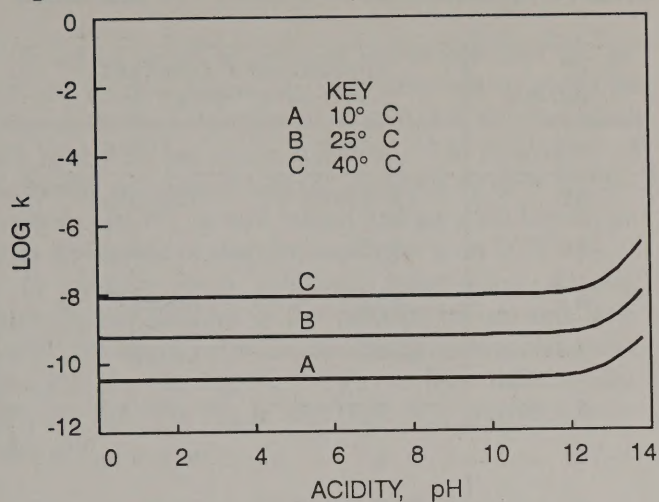
At  $\text{pH} < 8$ ,  $\{\text{CSNN}\}$  decomposes to  $\text{SCN}^-$  and  $\text{NH}_4^+$  (88). At  $\text{pH} > 12$ ,  $\{\text{CSNN}\}$  hydrolyzes to  $\text{SH}^-$  and presumably  $\text{OC}(\text{NH}_2)_2$  (99). The data are shown in table F-15 and figure 7-24. At pH 11.0 the half-life of  $\{\text{CSNN}\}$  varies from about 1,400 years at  $0^\circ\text{C}$  to about 20 years at  $40^\circ\text{C}$ .





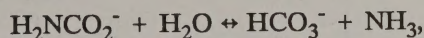


Figure 7-25

Log *k* versus pH for hydrolysis of urea.

### Carbamate

The equilibrium of {COON} with NH<sub>3</sub> and HCO<sub>3</sub><sup>-</sup> is rapid (minutes):



for which the equilibrium constant  $K = 0.5$  at 25° C (104-105). This equilibrium is significant only at pH 9 to 10, where HCO<sub>3</sub><sup>-</sup> and NH<sub>3</sub> are the predominant species in carbonate and ammonia solutions, respectively. The kinetic data were insufficient to elucidate a rate equation.

### Thiocarbonate

Thiocarbonate, {COOS}, rapidly hydrolyzes to {COOO} and SH<sup>-</sup> (108) with a half-life of 5 min in 5*M* NaOH at 25° C; the hydrolysis is faster at lower alkalinity.

## SUMMARY OF REACTIONS OF FREE CYANIDE AND DERIVED SPECIES

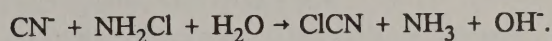
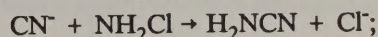
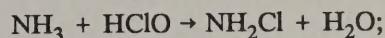
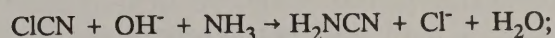
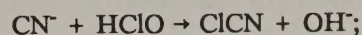
### Redox Reactions

The oxidations of {HCN} and derived species by ClO<sup>-</sup> and O<sub>3</sub> are as a rule very fast, and are complete in seconds to minutes. Oxidations by H<sub>2</sub>O<sub>2</sub> are generally slower, and require minutes to hours. Insufficient data were located for oxidations by HOOSO<sub>3</sub><sup>-</sup>, the presumed intermediate in the SO<sub>2</sub>-air process. Oxidations by O<sub>2</sub> are usually very slow and require days to years, unless catalysis occurs.

### Water Addition and Hydrolysis Reactions

The water addition and hydrolysis reactions of {HCN}, {NCCN}, and ClCN are the most important reactions that

remove these species, besides oxidation reactions. The end products of the water addition and hydrolysis reactions are respectively {HCOO}, {OCCOO}, and {COOO}. These reactions proceed with widely differing pH-dependent rates. A summary of reaction standard Gibbs energy changes and substrate half-lives at pH 11.0 is given in table 7-3. The correlation of standard Gibbs energy change and reaction rate is poor. The most slowly reacting species are {HCN}, {CNNN}, {CONN}, and {CSNN}. The formation of {CNNN}, {CONN}, and {CSNN} would be expected to require the presence of {CNN}, which could form via the oxidation of {HCN} in the presence of NH<sub>3</sub> by ClO<sup>-</sup>/HClO:



As described above, {CNN} reacts with H<sub>2</sub>O, NH<sub>3</sub> and H<sub>2</sub>S/SH<sup>-</sup> to form {CONN}, {CNNN} and {CSNN}, respectively. With the oxygen oxidants H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>, and HOOSO<sub>3</sub><sup>-</sup>, CN<sup>-</sup> is converted to NCO<sup>-</sup>, and no {CNN} is formed. Reaction of NCO<sup>-</sup> with NH<sub>3</sub> gives {CONN}, but there are no reactions of NCO<sup>-</sup> that form {CNNN} or {CSNN}.

### Other Reactions

#### Addition Reactions With Ammonia and Sulfide

Where NH<sub>3</sub> and H<sub>2</sub>S/SH<sup>-</sup> are present in solutions as a result of hydrolysis reactions or reactions of sulfide minerals, addition reactions of {HCN} and derived species with these reactants may occur. The species thus formed hydrolyze at different rates. Sulfur-containing species also undergo oxidation by O<sub>2</sub> or other oxidants. Volatilization of NH<sub>3</sub> and H<sub>2</sub>S and oxidation of sulfides compete with addition reactions.

#### Exchange Reactions

Exchange reactions of nitrogen- and sulfur-containing species with NH<sub>3</sub> and H<sub>2</sub>S/SH<sup>-</sup> are known to occur, but are not likely to be significant at the low concentrations prevailing in process and impounded solutions. Volatilization of NH<sub>3</sub> and H<sub>2</sub>S and oxidation of sulfides compete with exchange reactions.



Table 7-3.-Water addition hydrolysis and reactions of free cyanide and derived and related species

Reaction	$\Delta_r G^\circ$ , 25° C kJ·mol <sup>-1</sup> substrate	Approximate reactant half-life <sup>1</sup> at pH 11.0	
		0° C	40° C
$\text{CN}^- + 2\text{H}_2\text{O} \rightarrow \text{H-CO-NH}_2 + \text{OH}^-$	-36	80 years	120 days
$\text{H-CO-NH}_2 + \text{OH}^- \rightarrow \text{HCO}_2^- + \text{NH}_3$	-39	50 days	1.5 days
$\text{H-C(NH}_2)_2^+ + \text{OH}^- \rightarrow \text{H-CO-NH}_2 + \text{NH}_3$	N	days	hours
$\text{H-CS-NH}_2 + \text{OH}^- \rightarrow \text{H-CO-NH}_2 + \text{SH}^-$	N	days	hours
$\text{NC-CN} + \text{OH}^- \rightarrow \text{NC-CO-NH}^-$	N	3 s	0.10 s
$\text{NC-CN} + 2\text{OH}^- \rightarrow \text{CN}^- + \text{NCO}^- + \text{H}_2\text{O}$	-149	9 s	0.2 s
$\text{NC-CO-NH}^- + \text{OH}^- \rightarrow \text{CN}^- + \text{NCO}^- + \text{H}_2\text{O}$	N	1.1 min	0.3s
$\text{NC-CO-NH}^- + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{N-CO-CO-NH}_2 + \text{OH}^-$	N	months	days
$\text{H}_2\text{N-CO-CO-NH}_2 + \text{OH}^- \rightarrow \text{H}_2\text{N-CO-CO}_2^- + \text{NH}_3$	-35	2 days	5 h
$\text{H}_2\text{N-CO-CO}_2^- + \text{OH}^- \rightarrow \text{C}_2\text{O}_4^{2-} + \text{NH}_3$	-49	120 days	40 days
$\text{NC-C(NH}_2)_2^+ + 3\text{OH}^- \rightarrow \text{CN}^- + \text{HNCN}^- + 3\text{H}_2\text{O}$	N	minutes	seconds
$\text{NC-C(NH}_2)_2^+ + 2\text{OH}^- \rightarrow \text{NC-CO-NH}^- + \text{NH}_3 + \text{H}_2\text{O}$	N	days	hours
$\text{C}_2(\text{NH}_2)_4^{2+} + 2\text{OH}^- \rightarrow \text{H}_2\text{N-CO-CO-NH}_2 + 2\text{NH}_3$	N	days	hours
$\text{NC-CS-NH}^- + \text{OH}^- \rightarrow \text{CN}^- + \text{SCN}^- + \text{H}_2\text{O}$	N	minutes	seconds
$\text{NC-CS-NH}^- + \text{OH}^- \rightarrow \text{NC-CO-NH}^- + \text{SH}^-$	N	days	hours
$\text{H}_2\text{N-CS-CS-NH}_2 + \text{OH}^- \rightarrow \text{H}_2\text{N-CS-CO-NH}_2 + \text{SH}^-$	N	days	hours
$\text{H}_2\text{N-CS-CO-NH}_2 + \text{OH}^- \rightarrow \text{H}_2\text{N-CO-CO-NH}_2 + \text{SH}^-$	N	days	hours
$\text{ClCN} + 2\text{OH}^- \rightarrow \text{NCO}^- + \text{Cl}^- + \text{H}_2\text{O}$	-282	4 h	4 s
$\text{NCO}^- + \text{H}_2\text{O} \rightarrow \text{H}_2\text{N-CO}_2^-$	-44	50 years	70 days
$\text{H}_2\text{N-CO}_2^- + \text{OH}^- \rightarrow \text{CO}_3^{2-} + \text{NH}_3$	-19	minutes	seconds
$\text{HNCN}^- + 2\text{H}_2\text{O} \rightarrow \text{CO(NH}_2)_2 + \text{OH}^-$	-71	2 years	4 days
$\text{C(NH}_2)_3^+ + \text{OH}^- \rightarrow \text{CO(NH}_2)_2 + \text{NH}_3$	-60	150 years	1 year
$\text{CO(NH}_2)_2 + \text{OH}^- \rightarrow \text{H}_2\text{N-CO}_2^- + \text{NH}_3$	-44	5,000 years	2.5 years
$\text{CS(NH}_2)_2 + \text{OH}^- \rightarrow \text{CO(NH}_2)_2 + \text{SH}^-$	-52	1,400 years	22 years
$\text{CS(NH}_2)_2 + \text{OH}^- \rightarrow \text{NCS}^- + \text{NH}_3 + \text{H}_2\text{O}$	-32	$6 \times 10^6$ years	1,300 years

N No data.

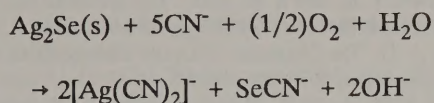
<sup>1</sup>Entries without numbers are rough estimates obtained from data for analogous reactions.



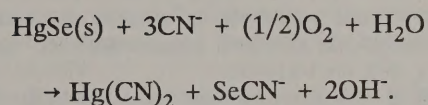
## SELENIUM IN CYANIDE PROCESS SOLUTIONS

Selenium occurs in precious metals ores and can be leached by cyanidation. In ores, selenium can exist in minerals that include heavy-metal selenides, metal selenites and selenates, and native selenium. The dissolution of elemental selenium in cyanide solutions to form selenocyanate, ( $\text{SeCN}^-$ ), is well known and parallels the analogous dissolution of elemental sulfur to form  $\text{SCN}^-$ .

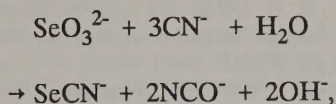
In cyanide leach solutions, heavy-metal selenide minerals can dissolve in the presence of air and form  $\text{SeCN}^-$ ; the heavy metal can dissolve as cyanide complexes ( $\text{Zn}$ ,  $\text{Cd}$ ,  $\text{Hg}$ ,  $\text{Cu}$ ,  $\text{Ag}$ ,  $\text{Ni}$ ,  $\text{Co}$ ,  $\text{Fe}$ ) or form oxide species ( $\text{Pb}$ ,  $\text{Sb}$ ,  $\text{Bi}$ ). For  $\text{Ag}_2\text{Se}$  and  $\text{HgSe}$ , the presumed reactions are



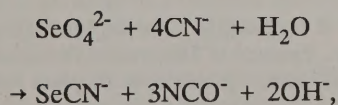
and



The alkaline cyanide solutions can leach selenite and selenate minerals to form dissolved  $\text{SeO}_3^{2-}$  and  $\text{SeO}_4^{2-}$  and metal cyanide or oxide species. From thermodynamic data (tables B-1 and C-1),  $\text{CN}^-$  is predicted to reduce  $\text{SeO}_3^{2-}$  and  $\text{SeO}_4^{2-}$  to  $\text{SeCN}^-$ ,



and



but the rates of these reactions are unknown. Equilibrium predominance area diagrams for selenium alone and in cyanide solutions are given in figures E-7 through E-9; these may be compared with the corresponding diagrams for sulfur in figures E-4 through E-6.

Little is known about the aqueous chemistry of  $\text{SeCN}^-$ . It forms insoluble salts with some heavy-metal ions and complexes with many metal ions analogous to the corresponding thiocyanate species (89, pp. 342-344). In acid solution,  $\text{SeCN}^-$  decomposes to selenium and  $\text{HCN}$ , as shown in figures E-8 and E-9, so  $\text{SeCN}^-$  may be classified

as a "weak-acid-dissociable" (WAD) cyanide. No information was located concerning oxidation of  $\text{SeCN}^-$ . As is the case with  $\text{SCN}^-$ , oxidants may attack the Se atom preferentially, with the formation of selenium oxide species and  $\text{CN}^-/\text{HCN}$ .

## CYANIDE DEGRADATION IN INDUSTRIAL PROCESSES

From data on industrial cyanide losses (17-18) and a review of the fate of cyanide in the environment (106), the pathways for loss or degradation of  $\text{CN}^-$  are

- Volatilization of  $\text{HCN}$ , e.g., via acidification by atmospheric  $\text{CO}_2$  [ $\text{CN}^- + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{HCN} + \text{HCO}_3^-$ ].
- Oxidation to  $\text{NCO}^-$ , and hydrolysis of  $\text{NCO}^-$  to  $\text{CO}_3^{2-}$  and  $\text{NH}_3$  or oxidation to  $\text{N}_2$  and  $\text{CO}_3^{2-}$ .
- Oxidation to  $\text{H}_2\text{NCN}$  in the presence of  $\text{NH}_3$ .
- Reaction with sulfur species to form  $\text{SCN}^-$ .
- Complexation or precipitation by metals such as iron and copper.
- Hydrolysis to  $\text{HCO}_2^-$  and  $\text{NH}_3$ .
- Adsorption on carbon, clays, soils, or biomass.
- Biodegradation.

Adams (17-18) studied cyanide losses in gold process solutions as a function of the concentration of suspended activated carbon. Data were given for a solution composition typical for carbon adsorption of gold, 0.008M  $\text{NaCN}$  at a pH of 10.2 and a temperature of 20° C, dosed with 25 g·L<sup>-1</sup> of fresh activated carbon. The data are not very consistent, but they indicate that the loss of  $\text{CN}^-$  from solution after 48 h was distributed approximately as follows:

Oxidized to $\text{NCO}^-$ . . . . .	35 pct
Volatilized as $\text{HCN}$ . . . . .	5 pct
Adsorbed on carbon . . . . .	25 pct
Hydrolyzed to $\text{HCO}_2^-$ and $\text{NH}_3$ . . . . .	0 pct
Total . . . . .	65 pct

The fate of the other 35 pct of  $\text{CN}^-$  was not reported. In control experiments without carbon, the total loss of  $\text{CN}^-$ , which was attributed to volatilization of  $\text{HCN}$ , was about 5 pct. As described above under cyanide oxidation, activated carbon catalyzes the oxidation of  $\text{CN}^-$  to  $\text{NCO}^-$  by  $\text{O}_2$ . There was a loss of about 10 pct of the  $\text{NCO}^-$ , which was assumed to be due to hydrolysis to  $\text{CO}_3^{2-}$  and  $\text{NH}_3$ . The rate data given above for the hydrolysis of  $\text{NCO}^-$  led to a predicted time for hydrolysis of 10 pct of the  $\text{NCO}^-$ , which is 1 to 2 powers of 10 longer than that observed by Adams, so catalysis of the hydrolysis of  $\text{NCO}^-$  by activated carbon is indicated. No formation of  $\text{HCO}_2^-$  was reported; this is consistent with the rate data described above, which



give a time of roughly 300 days for conversion of 1 pct of  $\text{CN}^-$  to  $\text{HCO}_2^-$ .

The engineering details of industrial practice for cyanide destruction and studies of the degradation of  $\text{CN}^-$  at closed mining and processing sites have been adequately reviewed elsewhere (107-108) and are not discussed further in this publication.

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<sup>2</sup>A title in parentheses is a translation from the language in which the work was published.



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## CHAPTER 8.—REACTIONS OF METAL CYANIDE SPECIES

### INTRODUCTION

The role of the cyanide chemistry of precious metals and associated accessory elements in the operation and closure of precious metals mines is the heart of this publication. The precious metals and accessory elements differ greatly in the formation and reactions of cyanide species, and this complicates the environmental fate and toxicity of cyanide. Chemical data on the formation and reactions of metal cyanide species are therefore critical to understanding and managing the environmental fate of cyanides.

This chapter discusses the chemistry of the metal cyanide complexes pertinent to mining, processing, and closure operations. Modern nomenclature, which is described in chapter 2, is used throughout. Much of the information is derived from a monograph by Sharpe (1),<sup>1</sup> or from thermodynamic data (2-4) that are detailed in appendix D. Additional information was obtained from primary sources as specified below.

The metals Zn, Cd, Hg, Cu, Ag, Au, Ni, Co, Fe, Mn, Cr, V, and Ti are discussed individually in the sections below after an initial overview. The subject of mixtures of metals in cyanide solutions is treated in chapter 10. The cyanides of the remaining elements are surveyed in chapter 3. All six platinum-group metals and Mo, W, and Re also form strong cyanide complexes (1). These are not discussed here because the reactions involved are slow and complex, few thermodynamic or kinetic data are available, and these metals are rarely reported in precious metals cyanide leaching operations.

The discussion in this chapter is limited to thermal, i.e., nonphotochemical, reactions. Photochemical reactions are discussed in chapter 9. As seen in the subsequent discussion, there is not much literature on the oxidative destruction of metal cyanide species.

### OVERVIEW AND CLASSIFICATION OF METAL CYANIDE SPECIES

In terms of equilibrium constants for their formation, many metal cyanide complexes are stronger than metal complexes with most other ligands, even ethylenediaminetetraacetate ( $H_4\text{edta}$ ) and related reagents (2-4). Some pertinent data are shown in table 8-1, which gives the formation constants for dissolved metal complexes with  $\text{CN}^-$ ,  $\text{OH}^-$ ,  $(\text{edta})^{4-}$ , and  $(\text{nta})^{3-}$  (nitrilotriacetate), and solid metal sulfides and oxide compounds. Calculations with the data in table 8-1 show that most metal oxide compounds and even some metal sulfides are soluble in alkali-metal cyanide solutions.

The reactions of the metal cyanide species with acids are of major importance. Metal cyanide species differ widely in their reactivity with acids to liberate HCN. As outlined in chapter 2, metals have been classified with respect to the reactivity of their cyanide complexes with acids as "weak-acid-dissociable" (WAD) or "non-weak-acid-dissociable" (non-WAD). As noted, this classification is oversimplified, and some metals are more accurately classified as "partially WAD." The details of the reactions of metal cyanide species with acids are described below and subsequently summarized.

Also of major importance are the reactions of metal cyanide species with oxidants, e.g., hypochlorite ( $\text{ClO}^-$ ), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), and ozone ( $\text{O}_3$ ). This oxidation chemistry is likewise discussed in the following sections and subsequently summarized.

Finally, two more sections discuss removal of metals from cyanide solutions by cementation and consider the complexing of metals by other ligands in the absence of sufficient  $\text{CN}^-$ .

### ZINC, CADMIUM, AND MERCURY

Reactions involving the cyanide complexes of Zn, Cd, and Hg are nearly all fast. The water solubilities of the binary cyanides  $\text{M}(\text{CN})_2$  with  $\text{M} = \text{Zn, Cd, or Hg}$ , are  $3 \times 10^{-5}$ , 0.1, and 0.4M, respectively, at 25° C. In solutions 0.01M in free  $\text{CN}^-$ , typical of precious metals leaching conditions, Zn, Cd, and Hg each exist as their soluble tetracyanometallates  $[\text{M}(\text{CN})_4]^{2-}$ . Acids totally and rapidly decompose the zinc and cadmium cyanide complexes to liberate HCN. Anionic  $\text{Hg}(\text{II})$  cyanide complexes are decomposed by acid to soluble  $\text{Hg}(\text{CN})_2$ , which is thermodynamically so stable that its decomposition by acid requires the presence of a strong ligand, precipitant, or oxidant, e.g.,  $\text{I}_2$ ,  $\text{H}_2\text{S}$ , or  $\text{Cl}_2$ . Soluble sulfides convert all of the Zn, Cd, and Hg cyanide complexes to the insoluble metal sulfides at all pH values with liberation of free  $\text{CN}^-/\text{HCN}$ .

Reaction of  $\text{Hg}(\text{I})$  compounds with  $\text{CN}^-$  results in disproportionation to metallic mercury and  $\text{Hg}(\text{II})$  cyanide complexes.

Mercury (II) cyanide forms complexes with other metal cyanide complexes, e.g., the hexacyanoferrates (II) and (III),  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$ . The log K (rate constant) values for the 1:1 complexes with the hexacyanoferrates are both about 2 (5).

Stable  $\text{Hg}(\text{II})$  species with both  $\text{CN}^-$  and  $\text{O}^{2-}$ ,  $\text{OH}^-$ ,  $\text{Cl}^-$ , and  $\text{SCN}^-$  (thiocyanate) are known; data are compiled in table D-5. The cyanide oxide  $\text{Hg}_2\text{O}(\text{CN})_2$  is less soluble in water,  $4 \times 10^{-3}\text{M}$  at 25° C, than  $\text{Hg}(\text{CN})_2$ . Mercury(II) cyanide forms complexes with other heavy-metal salts, in which it functions like an organic nitrile.

<sup>1</sup>Italic numbers in parentheses refer to items in the list of references at the end of this chapter.



Table 8-1.-Comparison of stability constants of metal complexes with cyanide and other ligands

$M^{q+}$	$M(CN)_n^{q-n}$		M oxide		$MS_{q/2}$ , $\log K^1$	$M(edta)^{q-4}$ , $\log K^2$	$M(nta)_2^{q-6}$ , $\log K^2$
	n	Log K	Formula	Log K			
Zn(II)	4	19.6	ZnO	16.7	25.4	16.5	14.2
Cd(II)	4	17.9	Cd(OH) <sub>2</sub>	14.4	28.1	16.5	14.4
Hg(II)	4	39.0	HgO	25.4	53.2	21.5	<sup>3</sup> 14.3
Cu(I)	3	27.0	CuO <sub>0.5</sub>	14.7	23.6	N	N
Ag(I)	2	20.5	AgO <sub>0.5</sub>	7.7	25.0	7.2	<sup>3</sup> 5.4
Cu(II)	4	22.6	CuO	20.4	37.4	18.8	17.5
Ni(II)	4	30.2	Ni(OH) <sub>2</sub>	17.2	24.1	18.4	16.3
Co(II)	5	23.	Co(OH) <sub>2</sub>	15.7	23.2	16.4	14.3
Fe(II)	6	35.4	Fe(OH) <sub>2</sub>	15.2	17.7	14.3	12.8
Mn(II)	6	10.	Mn(OH) <sub>2</sub>	12.8	14.0	13.9	10.9
Co(III)	6	73.	CoO(OH)	48.5	X	41.4	N
Fe(III)	6	42.3	FeO(OH)	41.7	X	25.1	24.3
Mn(III)	6	35.	MnO(OH)	42.2	X	25.3	N
Cr(III)	6	33.	CrO <sub>1.5</sub> · xH <sub>2</sub> O	32.	14.6	23.4	N

N No data.

X Compound does not exist.

<sup>1</sup>Reaction  $M^{q+} + (q/2)SH^- + (q/2)OH^- \rightarrow MS_{q/2} + (q/2)H_2O$ .<sup>2</sup>Ionic strength 0.1M.<sup>3</sup>1:1 complex.

Note.—Data for cyanides, sulfides, and oxides are from appendix D; data for other ligands are from Martell and Smith (2-4); edta = ethylenediamine tetraacetate; nta = nitrilotriacetate. Values are at 25° C and zero ionic strength unless stated otherwise.

Most of the foregoing information in this section is illustrated in the equilibrium predominance area diagrams (EPAD) in figures E-10 through E-74 in appendix E.

Zinc and cadmium cyanide complexes are decomposed via hydrolysis of CN<sup>-</sup> to metal hydroxides, ammonia (NH<sub>3</sub>), and formate (HCO<sub>2</sub><sup>-</sup>) at 150° to 200° C (6-7). They undergo oxidative destruction by ClO<sup>-</sup> (8-9; 10, p. 204), H<sub>2</sub>O<sub>2</sub> in the presence of copper catalyst (10, p. 239), SO<sub>2</sub>/air in the presence of copper catalyst (10, pp. 303-304), O<sub>3</sub> (11-12), or ClO<sub>2</sub> (13) to metal oxide products and cyanate (NCO<sup>-</sup>). Detailed systematic kinetics studies of these reactions have not been published. No literature on the oxidative destruction of mercury cyanide complexes was located. Cyanide complexes of mercury have been treated with metallic copper to cement mercury, and the resulting copper cyanide solution has been oxidized with H<sub>2</sub>O<sub>2</sub> (16).

## COPPER, SILVER, AND GOLD

Reactions involving the cyanide complexes of Cu, Ag, and Au in the 1+ oxidation state are usually fast. The binary cyanides, MCN with M = Cu, Ag, or Au, are all very insoluble in water. In solutions 0.01M in free CN<sup>-</sup> under precious metals leaching conditions, Cu, Ag, and Au exist only in the 1+ oxidation state and form the soluble complexes [Cu(CN)<sub>3</sub>]<sup>2-</sup>, [Ag(CN)<sub>2</sub>]<sup>-</sup>, and [Au(CN)<sub>2</sub>]<sup>-</sup>, respectively. The [Cu(CN)<sub>2</sub>]<sup>-</sup> complex predominates only at free CN<sup>-</sup> concentrations below about 10<sup>-5</sup>M. At free CN<sup>-</sup> concentrations above 0.01M to 0.1M, [Cu(CN)<sub>4</sub>]<sup>3-</sup>, [Ag(CN)<sub>3</sub>]<sup>2-</sup>, and [Ag(CN)<sub>4</sub>]<sup>3-</sup> predominate. The anionic cyanide complexes of copper and silver are rapidly decomposed by acids to the insoluble binary cyanides. For gold, this reaction is incomplete (15). Decomposition of

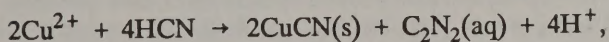


the binary cyanides MCN by acids requires a strong complexing or oxidizing agent, e.g., I or Cl<sub>2</sub>. Soluble sulfides precipitate silver sulfide (Ag<sub>2</sub>S) from solutions of its anionic cyanide complexes but do not react with the anionic Cu(I) or Au(I) cyanide complexes. However, H<sub>2</sub>S reacts with Cu(I) cyanides to form copper sulfide (Cu<sub>2</sub>S) and hydrogen cyanide (HCN) at pH below 8.

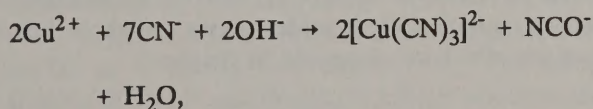
Few stable complexes containing both CN<sup>-</sup> and other inorganic ligands appear to exist for Cu(I) or Ag(I). The species [Ag(OH)(CN)]<sup>-</sup> exists in alkaline solutions (see appendix D). Complexes of Cu(I), Ag(I), and Au(I) with both CN<sup>-</sup> and S<sub>2</sub>O<sub>3</sub><sup>2-</sup> (thiosulfate) have been reported (16). The extent to which Au(I) forms complexes such as Au(CN)L, where L is a different inorganic ligand, has been little investigated. Only the iodocyanoaurate(I), [Au(CN)I]<sup>-</sup> was reported recently (17). However, judging by the log K data for this species and data for similar Hg(II) species (table D-5), species such as [Au(CN)Cl]<sup>-</sup> and [Au(CN)(SCN)]<sup>-</sup> may exist in solutions depleted of CN<sup>-</sup>.

Most of the foregoing information in this section is illustrated in the EPAD in figures E-75 through E-94 and E-101 through E-140.

Copper(II) cyanide complexes are unstable with respect to reduction of Cu(II). Cyanide rapidly reduces Cu(II) to Cu(I), and is itself oxidized to cyanogen (C<sub>2</sub>N<sub>2</sub> in acid solution or to NCO<sup>-</sup> in basic solution. When Cu(II) is added to excess alkaline cyanide solution, the violet [Cu(CN)<sub>4</sub>]<sup>2-</sup> forms transiently (18-19). For the reaction



log K = +15.5 at 25° C. For the reaction



log K = +93.4 at 25° C. The log K values for these reactions are so large that there is no known complexing agent for Cu(II) that will prevent the reduction of Cu(II) by CN<sup>-</sup> (2-4); see tables 8-1, D-6, and D-7. However, CuCN and solutions of Cu(I) cyanide complexes with mole ratio CN<sup>-</sup> to Cu(I) < 3 in the presence of NH<sub>3</sub> or organic amines undergo slow oxidation by atmospheric O<sub>2</sub> to form ternary complexes that are polymeric cyanocuprate(I) salts of Cu(II) complexes with NH<sub>3</sub> or organic amine (1, 20). The complex [Cu(edta)]<sup>2-</sup>, reacts with CN<sup>-</sup> to form [Cu(edta)(CN)]<sup>3-</sup> with a log K value of about +4 (21). However, this complex undergoes significant decomposition during 1 day. Although Cu(II) is readily reduced by free CN<sup>-</sup>, reduction by complexed CN<sup>-</sup> in [Cu(CN)<sub>3</sub>]<sup>2-</sup> or [Cu(CN)<sub>5</sub>]<sup>3-</sup> appears to be slow.

Reactions of Au(III) complexes are generally slow. The colorless tetracyanoaurate(III), [Au(CN)<sub>4</sub>]<sup>-</sup>, can be formed by reaction of Au(III) compounds with CN<sup>-</sup>. It is not decomposed by acids; the solid acid H[Au(CN)<sub>4</sub>]·xH<sub>2</sub>O can be isolated. Gold(III) complexes with both CN<sup>-</sup> and other ligands, e.g., [Au(CN)<sub>2</sub>Cl]<sup>-</sup>. Data for such species are compiled in table D-10. The [Au(CN)<sub>4</sub>]<sup>-</sup> species is reported to form by anodic oxidation in cyanide gold-plating baths, but has not been reported to form during gold leaching. It can be reduced to [Au(CN)<sub>2</sub>]<sup>-</sup> by N<sub>2</sub>H<sub>4</sub> (22).

The cyanide complexes of copper are decomposed via hydrolysis of the CN<sup>-</sup> to copper oxides, NH<sub>3</sub>, and HCO<sub>2</sub><sup>-</sup> at 150° to 200° C (6). They undergo oxidative destruction by ClO<sup>-</sup> (8-9; 10, p. 204), H<sub>2</sub>O<sub>2</sub> (10, p. 239), SO<sub>2</sub>/air (10, pp. 303-304), O<sub>3</sub> (12-13, 23), or ClO<sub>2</sub> (chlorine dioxide) (13), to metal oxide products and NCO<sup>-</sup>. Detailed systematic kinetics studies of these reactions have not been published. Oxygen is reported to oxidize Cu(I) cyanide complexes in the presence of activated carbon (24).

Silver cyanide complexes are incompletely destroyed by ClO<sup>-</sup> (8-9) but are reported to be completely destroyed by O<sub>3</sub> (11). No information on the oxidation of silver cyanide species by H<sub>2</sub>O<sub>2</sub> or SO<sub>2</sub>/air was located. Reaction of silver cyanide complexes with metallic copper to cement silver, followed by H<sub>2</sub>O<sub>2</sub> oxidation of the copper cyanide species was reported (14).

Gold cyanide complexes are reported to precipitate AuCN on reaction with O<sub>3</sub> (11). No data were located regarding the reactions of gold cyanide species with other oxidants.

## NICKEL

Reactions of Ni(II) complexes are usually fast. The only important nickel species in dilute cyanide solutions is the orange-yellow tetracyanonickelate(II), [Ni(CN)<sub>4</sub>]<sup>2-</sup>. The kinetics of formation of [Ni(CN)<sub>4</sub>]<sup>2-</sup> from Ni<sup>2+</sup> and CN<sup>-</sup>, and the total decomposition of [Ni(CN)<sub>4</sub>]<sup>2-</sup> by acid with liberation of HCN, both of which are rapid, have been studied (25-28). Researchers studying the latter (25-26) inferred the formation of protonated species, e.g., [HNi(CN)<sub>4</sub>]<sup>-</sup>, but in a subsequent reinvestigation, the data were interpreted without formation of protonated species (27). The acid H<sub>2</sub>[Ni(CN)<sub>4</sub>] is not isolable and is probably strong, i.e., completely dissociated. Intermediate species such as [Ni(CN)<sub>3</sub>]<sup>-</sup> are evidently not stable and disproportionate to Ni<sup>2+</sup> and [Ni(CN)<sub>4</sub>]<sup>2-</sup>.

In solutions with free CN<sup>-</sup> exceeding 1M, [Ni(CN)<sub>4</sub>]<sup>2-</sup> is incompletely converted to orange-red pentacyanonickelate(II), [Ni(CN)<sub>5</sub>]<sup>3-</sup>.

Examples of relatively slow reactions of Ni(II) are the reactions of CN<sup>-</sup> with Ni(II) complexes of polyamines, e.g., triethylenetetramine, or aminopolycarboxylates, e.g., edta.



The reverse reactions of  $[\text{Ni}(\text{CN})_4]^{2-}$  with such ligands, which occur in nearly neutral solutions, are also slow.

The addition of soluble sulfides to  $[\text{Ni}(\text{CN})_4]^{2-}$  solutions does not precipitate  $\text{NiS}$ .

Most of the foregoing information in this section is illustrated in the EPAD in figures E-141 through E-162.

Cyanide complexes of  $\text{Ni(I)}$  and  $\text{Ni(O)}$  are known, but their preparation requires strongly reducing conditions, and they are very readily oxidized. Thus, they are not expected to occur in hydrometallurgical processes.

Nickel(III) cyanide complexes are reported to occur as unstable intermediates in the oxidation of  $[\text{Ni}(\text{CN})_4]^{2-}$  by  $\text{Cl}_2$  or  $\text{HClO}$  (29).

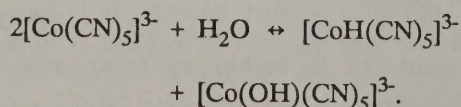
Tetracyanonickelate(II) decomposes via hydrolysis of the  $\text{CN}^-$  to  $\text{Ni(OH)}_2$ ,  $\text{NH}_3$ , and  $\text{HCO}_2^-$  at  $150^\circ$  to  $200^\circ \text{C}$  (6,30-31). It is also oxidized by  $\text{ClO}^-$  (9; 10, p. 204),  $\text{H}_2\text{O}_2$  in the presence of copper catalyst (10, p. 239),  $\text{SO}_2/\text{air}$  in the presence of copper catalyst (10, pp. 303-304), or  $\text{O}_3$  (11-12, 23), but not by  $\text{ClO}_2$  (13). The reaction with  $\text{ClO}^-$  is slower than the corresponding reactions with the zinc and cadmium cyanide complexes. The reaction of  $[\text{Ni}(\text{CN})_4]^{2-}$  with  $\text{O}_3$  is reported to be fast. Detailed systematic kinetics studies of these reactions have not been published.

Recently, a reaction of  $[\text{Ni}(\text{CN})_4]^{2-}$  in a polysulfide solution to form a  $\text{Ni(II)}$  polysulfide complex,  $[\text{Ni}(\text{S}_4)_2]^{2-}$ , was reported (32). The reaction occurred in minutes at room temperature. The fate of the  $\text{CN}^-$  was not stated, but presumably the  $\text{CN}^-$  was converted to  $\text{SCN}^-$ .

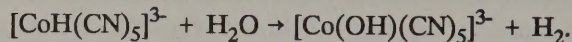
## COBALT

Reactions of  $\text{Co(II)}$  complexes are usually fast; reactions of  $\text{Co(III)}$  complexes are usually slow. The cyanide chemistry of cobalt is unusual in that  $\text{Co(II)}$  cyanide complexes are very easily oxidized to  $\text{Co(III)}$  cyanide complexes, so that in mining and metallurgical situations, cobalt minerals leached by cyanide solutions will be rapidly oxidized by air to  $\text{Co(III)}$ .

Reaction of  $\text{Co}^{2+}$  with  $\text{CN}^-$  in the absence of oxygen gives olive-green pentacyanocobaltate(II),  $[\text{Co}(\text{CN})_5]^{3-}$ , which is in equilibrium with a violet dimer  $[\text{Co}_2(\text{CN})_{10}]^{6-}$ . This complex reacts with  $\text{H}_2\text{O}$  to give an equilibrium involving the colorless hydridopentacyanocobaltate(III),  $[\text{CoH}(\text{CN})_5]^{3-}$ , and the yellow hydroxopentacyanocobaltate(III),  $[\text{Co(OH)}(\text{CN})_5]^{3-}$ :



The hydrido complex is readily oxidized by  $\text{O}_2$ . It also reacts slowly with water:



Pentacyanocobaltate(II) also reacts rapidly with  $\text{O}_2$  to form the intermediate superoxopentacyanocobaltate(III)  $[\text{Co}(\text{CN})_5(\text{O}_2)]^{3-}$ , which hydrolyzes to  $[\text{Co(OH)}(\text{CN})_5]^{3-}$  or forms hexacyanocobaltate(III),  $[\text{Co}(\text{CN})_6]^{3-}$  if free  $\text{CN}^-$  is present. Pentacyanocobaltate(II) is rapidly and completely decomposed by acids, with liberation of  $\text{HCN}$  (33).

The pale yellow hexacyanocobaltate(III) is a very inert species; the free acid  $\text{H}_3[\text{Co}(\text{CN})_6]$  is stable and isolable as a soluble solid. The only known means of decomposition of  $[\text{Co}(\text{CN})_6]^{3-}$  in aqueous solution is by photochemistry, which is described in chapter 9.

The chemistry of the yellow  $[\text{Co(OH)}(\text{CN})_5]^{3-}$  and  $[\text{Co(H}_2\text{O)}(\text{CN})_5]^{2-}$  derived by protonation (pH below 9) has not been adequately investigated. There is evidence that these complexes slowly polymerize at moderate concentrations, perhaps in a way similar to that of the corresponding ion complexes (see below). Aquopentacyanocobaltate(III) undergoes substitution of the water by  $\text{CN}^-$ ,  $\text{Cl}^-$ ,  $\text{NH}_3$ ,  $\text{NCS}^-$ , or other species, and the kinetics of many of these reactions have been determined (34-37). Data are presented in table 8-2. These reactions are catalyzed by  $[\text{Co}(\text{CN})_5]^{3-}$ , the presence of which requires the absence of  $\text{O}_2$ .

Tetracyano and tricyano complexes of  $\text{Co(III)}$  have been obtained photochemically (38-39) (see chapter 9). These species polymerize to unidentified products unless their concentrations are below  $10^{-3}M$ .

Hexacyanocobaltate(III) is not destroyed by  $\text{ClO}^-$  (10, p.204),  $\text{O}_3$  (11-12) or  $\text{ClO}_2$  (13). The only known routes to destruction of  $\text{Co(III)}$  cyanide species are photochemical reactions, which are discussed in chapter 9.

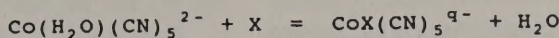
## IRON

Although the reactions of most  $\text{Fe(II)}$  and  $\text{Fe(III)}$  complexes are fast, the reactions of  $\text{Fe(II)}$  and  $\text{Fe(III)}$  cyanide complexes are usually slow. The light-yellow hexacyanoferrate(II) (ferrocyanide),  $[\text{Fe}(\text{CN})_6]^{4-}$ , and deep yellow to red-orange hexacyanoferrate(III) (ferricyanide),  $[\text{Fe}(\text{CN})_6]^{3-}$ , are among the best known of all metal cyanide complexes. They are both thermodynamically unstable with respect to decomposition by acids; however the rates of decomposition by acid are so slow that the free acids  $\text{H}_4[\text{Fe}(\text{CN})_6]$  and  $\text{H}_3[\text{Fe}(\text{CN})_6]$  are isolable as soluble solids.



Table 8-2.-Substitution reactions of pentacyanocobaltates(III)

(All data at 40° C and ionic strength 1.0M)



$$\text{Forward rate: } -d[\text{Co}(\text{H}_2\text{O})(\text{CN})_5^{2-}]/dt = k_f[\text{Co}(\text{H}_2\text{O})(\text{CN})_5^{2-}][\text{X}]$$

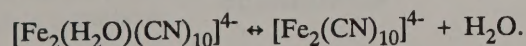
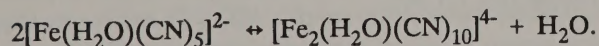
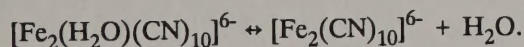
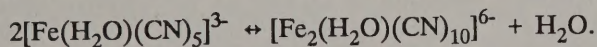
$$\text{Reverse rate: } -d[\text{CoX}(\text{CN})_5^{q-}]/dt = k_r[\text{CoX}(\text{CN})_5^{q-}]$$

X	$k_f, \text{M}^{-1} \text{s}^{-1}$	$k_r, \text{s}^{-1}$	References
$\text{CN}^-$	$1.2 \times 10^{-4}$	N	34
Cl	$5.5 \times 10^{-4}$	$4.5 \times 10^{-4}$	36
$\text{NH}_3$	$2.1 \times 10^{-4}$	N	37
$\text{NCS}^-$	$6.3 \times 10^{-4}$	$3.7 \times 10^{-7}$	34-35

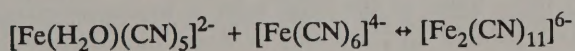
N No data.

Reaction of iron salts with  $\text{CN}^-$  in aqueous solution cannot be stopped at any intermediate soluble complexes; the hexacyanoferrates are always formed. The reaction of Fe(II) salts with  $\text{CN}^-$  to form  $[\text{Fe}(\text{CN})_6]^{4-}$  is rapid, and  $[\text{Fe}(\text{CN})_6]^{4-}$  can be oxidized to  $[\text{Fe}(\text{CN})_6]^{3-}$  at a rate which depends on pH and the oxidant used. The reaction of Fe(III) salts with  $\text{CN}^-$  does not as readily form  $[\text{Fe}(\text{CN})_6]^{3-}$  because hydrous Fe(III) oxide forms first because of the high pH. The hydrous Fe(III) oxide reacts slowly with  $\text{CN}^-$  to form  $[\text{Fe}(\text{CN})_6]^{4-}$  as well as  $[\text{Fe}(\text{CN})_6]^{3-}$ , because  $\text{CN}^-$  slowly reduces the Fe(III) species. From thermodynamic data, reaction of Fe(III) salts with  $\text{CN}^-$  in acid solution should yield Fe(II) and  $\text{C}_2\text{N}_2$ , but this reaction seems not to have been documented.

The yellow, hydroxopentacyanoferrates and aquopentacyanoferrates,  $[\text{Fe}(\text{OH})(\text{CN})_5]^{3-}$ ,  $[\text{Fe}(\text{H}_2\text{O})(\text{CN})_5]^{3-}$ , and  $[\text{Fe}(\text{H}_2\text{O})(\text{CN})_5]^{2-}$ , are obtainable only by photochemistry so far as is known (see chapter 9). The complexes  $[\text{Fe}(\text{H}_2\text{O})(\text{CN})_5]^{3-}$  and  $[\text{Fe}(\text{H}_2\text{O})(\text{CN})_5]^{2-}$  are deprotonated to the respective hydroxo complexes above pH about 14 and pH about 9, respectively. These complexes exist in slow equilibria via condensation reactions to form the aquodecacyanodiferrates and decacyanodiferrates:



They also react with the hexacyanoferrates to form the undecacyanoferrates; e.g.,

+  $\text{H}_2\text{O}$ .

Most of the dinuclear complexes, namely with two Fe(II), one Fe(II) and one Fe(III), or two Fe(III), are known. However, characterization of their solution chemistry has not been sufficiently elucidated, and spectroscopic data from different authors disagree (see chapter 5). The oxodecacyanodiferrates,  $[\text{Fe}_2\text{O}(\text{CN})_{10}]^{4-}$ , may also exist, in analogy with a manganese analog mentioned below.

Published equilibrium data for the dinuclear iron cyanide species disagree (40-45); for this reason the dinuclear species were not included in the thermodynamic data in appendix D. Figures 8-1 and 8-2 summarize the relationships among the iron cyanide species. Rough but self-consistent values of pertinent equilibrium constants and reduction potentials are given in figures 8-1 and 8-2. Despite the limited accuracy of the data, it may be concluded that the pentacyanoferrate species and their condensation products are all unstable with respect to redistribution to hexacyanoferrates and iron cyanide precipitates. Consequently, they would not appear on EPAD and figures E-165, E-167, and E-168 represent true equilibrium conditions.

The aquopentacyanoferrates undergo substitution of  $\text{H}_2\text{O}$  by other reagents, e.g.,  $\text{CN}^-$ ,  $\text{NH}_3$ ,  $\text{SO}_3^{2-}$ ; the kinetics of several such reactions have been studied (42, 46-54). Some data for  $[\text{Fe}(\text{H}_2\text{O})(\text{CN})_5]^{3-}$  are compiled in table 8-3. Similar reactions of  $[\text{Fe}(\text{H}_2\text{O})(\text{CN})_5]^{2-}$  are much slower and subject to catalysis by  $[\text{Fe}(\text{H}_2\text{O})(\text{CN})_5]^{3-}$  (48, 50, 54); this fact was not realized in earlier work (46).

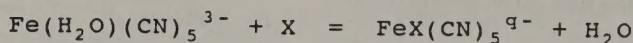
A few substitution or addition reactions of dinuclear iron cyanide species with reagents of no metallurgical interest have been studied (41, 43, 55).

The aquopentacyanoferrates both decompose to the respective hexacyanoferrates and cationic iron species, which cause precipitates to form (56-57).



Table 8-3.--Substitution reactions of pentacyanoferrates(II)

(All data at 25° C and ionic strength 1.0M)

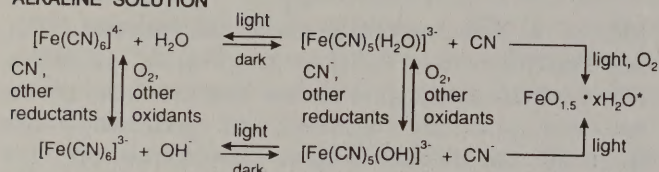
Forward rate:  $-\text{d}[\text{Fe}(\text{H}_2\text{O})(\text{CN})_5^{3-}]/\text{dt} = k_f[\text{Fe}(\text{H}_2\text{O})(\text{CN})_5^{3-}][\text{X}]$ Reverse rate:  $-\text{d}[\text{FeX}(\text{CN})_5^{q-}]/\text{dt} = k_r[\text{FeX}(\text{CN})_5^{q-}]$ 

X	$k_f, \text{M}^{-1} \text{s}^{-1}$	$k_r, \text{s}^{-1}$	References
$\text{CN}^-$	1.5	$3. \times 10^{-8}$	53
$\text{NH}_3$	$1.9 \times 10^2$	$1.8 \times 10^{-2}$	47-48, 51-52
$\text{SO}_3^{2-}$	3.3	$^{11} 1.3 \times 10^{-3}$	42, 49

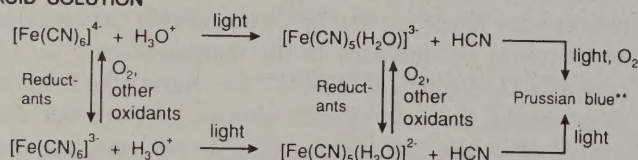
<sup>1</sup> Ionic strength 0.015M.

Figure 8-1

## ALKALINE SOLUTION

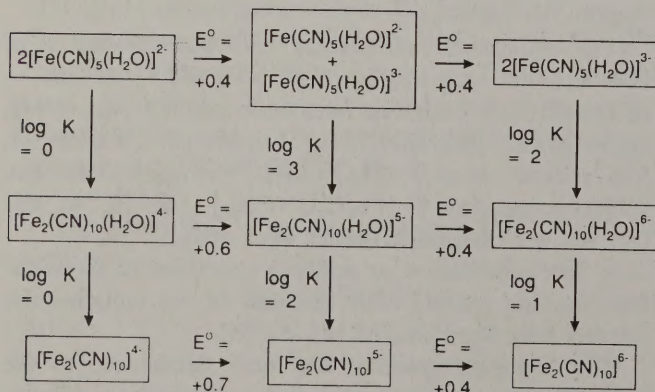
\* +  $\text{CN}^-$ ,  $\text{NCO}^-$  (? , via Fe(III) species,  $\text{O}_2$  ?)

## ACID SOLUTION

\*\* +  $\text{HCN}$ ,  $\text{C}_2\text{N}_2$  (? , via Fe(III) species; hydrolyzes? ),  
 $\text{NCO}^-$  (? , via Fe(III) species,  $\rightarrow \text{CO}_2 + \text{NH}^+$ )

## Formation of aquodecacyanoferrate and decacyanoferrate species.

Figure 8-2



## Formation of undecacyanoferrate species.

Oxidation of  $[\text{Fe}(\text{CN})_6]^{4-}$  to  $[\text{Fe}(\text{CN})_6]^{3-}$  by  $\text{HClO}$  (58),  $\text{ClO}_2$  (59),  $\text{H}_2\text{O}_2$  (60), and  $\text{O}_2$  (61) has recently been studied. Hydrogen peroxide reduces  $[\text{Fe}(\text{CN})_6]^{3-}$  to  $[\text{Fe}(\text{CN})_6]^{4-}$  in basic solution, but oxidizes  $[\text{Fe}(\text{CN})_6]^{4-}$  to  $[\text{Fe}(\text{CN})_6]^{3-}$  in acid solution. The oxidation of  $[\text{Fe}(\text{H}_2\text{O})(\text{CN})_5]^{3-}$  to  $[\text{Fe}(\text{H}_2\text{O})(\text{CN})_5]^{2+}$  by  $\text{H}_2\text{O}_2$  (62) and  $\text{O}_2$  (63) has been studied. The reaction with  $\text{O}_2$  is catalyzed by  $\text{Fe}^{2+}$ .

Free cyanide reduces  $[\text{Fe}(\text{CN})_6]^{3-}$  to  $[\text{Fe}(\text{CN})_6]^{4-}$  slowly; the reaction is strongly catalyzed by copper and has a complex mechanism (64-65).

The hexacyanoferrates decompose to iron oxides,  $\text{NH}_3$ , and  $\text{HCO}_2^-$  ( $\text{CN}^-$  hydrolysis) at 150-200° C (6). Destructive oxidation by  $\text{ClO}^-$  (10, p. 204),  $\text{O}_3$  (11-12), or  $\text{ClO}_2$  (13) is nonexistent or slow in the absence of ultraviolet irradiation. It is reported that  $\text{BrO}^-$  destructively oxidizes  $[\text{Fe}(\text{CN})_6]^{3-}$  at 75° C;  $\text{ClO}^-$  is much less effective (66). Effective destruction of iron cyanide species requires photochemical reactions; these are discussed in chapter 9.

Much of the published kinetic, equilibrium, and spectroscopic data for iron cyanide complexes, especially the aquopentacyano and dinuclear complexes, contain conflicting results. These have been attributed to failure to allow for the condensation reactions (40, 56, 67-68), failure to protect against oxidation by  $\text{O}_2$  (56, 63, 67) catalysis effects (48, 50, 63), unstable or impure reagents (40-41, 51, 68), spectrophotometric observations limited to only one wavelength (69), and failure to protect against photochemical reactions (60, 67, 69).

## MANGANESE

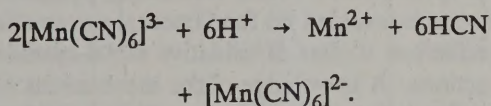
The chemistry of cyanide complexes of manganese, especially in aqueous solution, has not been adequately characterized. Reactions of  $\text{Mn(II)}$  complexes are generally fast. Some of the solid salts of hexacyanomanganate(II),  $[\text{Mn}(\text{CN})_6]^{4-}$ , are blue to violet, but whether this



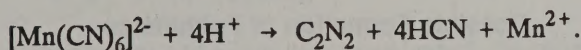
species exists in solutions of  $\text{Mn}^{2+}$  and  $\text{CN}^-$  has not been definitively demonstrated. Manganese(II) cyanide complexes are totally and rapidly decomposed by acids with liberation of  $\text{HCN}$ , therefore they fall in the WAD classification.

Solutions of  $\text{Mn}^{2+}$  and  $\text{CN}^-$  are oxidizable, e.g., by  $\text{O}_2$ , to  $\text{Mn(III)}$  cyanide complexes. Potassium hexacyanomanganate(III),  $\text{K}_3[\text{Mn(CN)}_6]$ , is a well-known red salt; its dilute aqueous solution decomposes, precipitating hydrous manganese oxides. Hydroxocyanomanganates or oxocyanomanganates exist; reddish-brown oxododecacyanodimanganate(III),  $[\text{Mn}_2\text{O(CN)}_{10}]^{6-}$  has been characterized in the solid state. Published data on the solution chemistry of manganese cyanide complexes are contradictory and show that the system is complex, with hydrolysis and disproportionation reactions occurring (70-77). A dinuclear complex, presumably  $[\text{Mn}_2\text{O(CN)}_{10}]^{6-}$ , was reported to be oxidizable in two one-electron steps to  $\text{Mn(III)Mn(IV)}$  and  $\text{Mn(IV)}_2$  species; the oxidized species undergo reduction by  $\text{CN}^-$  to the  $\text{Mn(III)}_2$  species (75).

Addition of acid (pH 0 to 1) to solutions of  $[\text{Mn(CN)}_6]^{3-}$  results in decomposition in minutes to  $\text{Mn}^{2+}$ ,  $\text{HCN}$ , and the unstable hexacyanomanganate(IV),  $[\text{Mn(CN)}_6]^{2-}$  (76-77).



At pH 0 to 1,  $[\text{Mn(CN)}_6]^{2-}$  decomposes in hours to  $\text{C}_2\text{N}_2$ ,  $\text{HCN}$ , and  $\text{Mn}^{2+}$  (79):



The reaction is catalyzed by product  $\text{Mn}^{2+}$ . At higher pH values,  $[\text{Mn(CN)}_6]^{3-}$  and  $[\text{Mn(CN)}_6]^{2-}$  hydrolyze to manganese oxides. Accordingly, the  $\text{Mn(III)}$  and  $\text{Mn(IV)}$  cyanide complexes may be classified as WAD.

In solution,  $\text{MnO}_4^-$  is rapidly reduced by  $\text{CN}^-$  to form manganese cyanide complexes.

The oxidation of cyanomanganates to  $\text{MnO}_2$  and  $\text{NCO}^-$  by  $\text{O}_2$  has not been demonstrated. Considering that  $\text{MnO}_2$  is thermodynamically capable of oxidizing  $\text{CN}^-$ , manganese oxides may possibly catalyze the oxidation of  $\text{CN}^-$  by  $\text{O}_2$ . As noted above, the  $\text{Mn(IV)}$ -containing dinuclear cyanide complexes oxidize  $\text{CN}^-$  (75). No literature was located that specifically addressed oxidative destruction of manganese cyanide complexes.

## CHROMIUM

Reactions of  $\text{Cr(III)}$  complexes are usually slow. Chromium(III) cyanide complexes are formed along with

hydrous  $\text{Cr}_2\text{O}_3$  when  $\text{Cr(III)}$  salts react with  $\text{CN}^-$ . The yellow hexacyanochromate(III),  $[\text{Cr(CN)}_6]^{3-}$ , is decomposed to hydrous  $\text{Cr}_2\text{O}_3$  in hot solutions. It is decomposed completely by acids with liberation of  $\text{HCN}$ , but at a rate slow enough to permit characterization of the intermediate aquocyno or hydroxocyno complexes (78). Accordingly,  $\text{Cr(III)}$  cyanide species may be classified as WAD, but complete decomposition requires days at  $25^\circ\text{C}$  and pH 2 (78-79). These reactions are catalyzed by  $\text{Cr(II)}$ , which requires the absence of  $\text{O}_2$  (80).

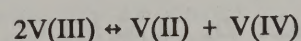
Chromium(II) cyanide complexes, e.g. hexacyanochromate(II),  $[\text{Cr(CN)}_6]^{4-}$ , exist only under strongly reducing conditions in the absence of  $\text{O}_2$  (81).

A  $\text{Cr(IV)}$  peroxocyno complex,  $[\text{Cr(O)}_2(\text{CN})_3]^{3-}$ , is known in the solid state, but practically nothing is known about its solution chemistry.

The only information located on nonphotochemical oxidative destruction of chromium cyanide complexes was an unsubstantiated claim that  $\text{H}_2\text{O}_2$  oxidizes  $\text{Cr(III)}$  cyanide complexes to  $\text{CrO}_4^{2-}$  in alkaline solution (82). Photochemical reactions that destroy  $\text{Cr(III)}$  cyanide species are discussed in chapter 9.

## VANADIUM

Reactions of vanadium complexes are generally fast. Vanadium forms cyanide complexes in the 2+, 3+, and 4+ oxidation states. The yellow-brown hexacyanovanadate(II),  $[\text{V(CN)}_6]^{4-}$ , the red heptacyanovanadate(III),  $[\text{V(CN)}_7]^{3-}$ , and the green oxopentacyanovanadate(IV),  $[\text{VO(CN)}_5]^{3-}$ , have been characterized in the solid state. Their solution chemistry is complex because disproportionation equilibria occur (83):



At least one other complex of unknown composition exists in cyanovanadate solutions (83). The reactivity of the cyanovanadates with acids has not been documented, and no thermodynamic data exist. If the cyanovanadates fit the trend of lower stability of cyanide complexes of transition metals on moving leftward in the periodic table, they are probably all WAD. Cyanide concentrations above 1M are required to maintain  $[\text{V(CN)}_7]^{3-}$  in solution (83).

The  $\text{V(II)}$  and  $\text{V(III)}$  cyanide complexes are readily oxidized by  $\text{O}_2$  to  $\text{V(IV)}$  species (83). Vanadium(IV) in alkaline solution is easily oxidized by  $\text{O}_2$  to vanadates(V); the same is probably true of  $\text{V(IV)}$  cyanide species. Vanadium(V) appears not to form cyanide complexes. Whether vanadate(V) and cyanide form cyanovanadate(IV) species via a redox reaction has not been investigated. Such a reaction, if it occurs, coupled with reoxidation of the cyanovanadate(IV) species by  $\text{O}_2$ , would constitute a vanadium-catalyzed oxidation of  $\text{CN}^-$  by  $\text{O}_2$ .



## TITANIUM

Attempts to obtain cyanotitanates from aqueous solutions give only hydrous oxides. Complex salts, e.g.,  $\text{Cs}_4\text{Ti}(\text{CN})_7$ , were reported to be obtained in nonaqueous preparations, but they are decomposed by water (84).

### SUMMARY OF METAL CYANIDE DESTRUCTION REACTIONS

The reactivity of metal cyanide species toward different reagents that may decompose them was discussed in the preceding sections. This section provides a summary of the nonoxidative and oxidative reactions that decompose metal cyanide species.

#### Nonoxidative Reactions

The reactivity of metal cyanide complexes toward decomposition by reagents that are not oxidants is summarized in table 8-4. In table 8-4, reactions with acids and sulfides are compiled and the metal cyanide complexes are classified as WAD, partially WAD (part-WAD), or non-WAD. No other common or inexpensive precipitants or complexing agents are listed, because they do not react with the metal cyanide complexes. Even ethylenediaminetetraacetate, one of the strongest complexing agents, does not displace  $\text{CN}^-$  from metal cyanide complexes in alkaline solution, as shown by calculations with the data in table 8-1.

From table 8-4, the thermodynamic data in appendix D, and the EPAD in appendix E, a more accurate classification is as follows:

WAD: Zn, Cd, Ni, Mn, Cr.

Partially WAD: Hg, Cu, Ag, Au(I).

Non-WAD: Au(III), Co, Fe.

The diagrams in appendix E clearly illustrate the distinction between WAD and partially WAD metal cyanide species. Compare, e.g., figures E-11, E-33, E-54, E-75, E-101, E-122, and E-142. These are pM-pH diagrams that show the predominant species at a free cyanide activity of  $10^{-5}M$  for Zn, Cd, Hg, Cu(I), Ag, Au(I), and Ni, respectively. At pH below 6, the predominant species of the respective metals are  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}(\text{CN})_2(\text{aq})$ ,  $\text{CuCN}(\text{s})$ ,  $[\text{Ag}(\text{CN})_2]^-$  and  $\text{AgCN}(\text{s})$ ,  $[\text{Au}(\text{CN})_2]^-$  and  $\text{AuCN}(\text{s})$ , and  $\text{Ni}^{2+}$ .

Some metal cyanide complexes are so stable that alkaline sulfides do not precipitate the metal sulfide; this is the case for Cu, Au, Ni, Co, and Fe. For copper and nickel, the metal sulfides and HCN are obtained at pH below 7

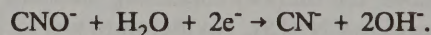
by using  $\text{H}_2\text{S}$ . For Mn(II) and Mn(III), sulfides are expected to precipitate  $\text{MnS}$ ; Mn(III) is reduced. Chromium(III) sulfide is not formed even from  $\text{Cr}^{3+}$  and sulfides, so its formation from chromium cyanide species is not expected. Equilibrium predominance area diagrams for metal cyanide species in the presence of sulfide are given in figures E-18, E-40, E-61, E-81, E-108, and E-149.

#### Oxidative Reactions

Table 8-5 summarizes reactions for the oxidative destruction of metal cyanide species. Many of the entries are predictions based on thermodynamic data. The reactions involve oxidation of  $\text{CN}^-$  to  $\text{NCO}^-$ , which in turn hydrolyzes slowly to  $\text{CO}_3^{2-}$  and  $\text{NH}_3$  or may be further oxidized to  $\text{CO}_3^{2-}$  and  $\text{N}_2$ , as discussed in chapter 7. In most cases, the metal product is known or expected to be an oxide species. The oxidative destruction of cyanide complexes of Zn, Cd, Cu, Ag, and Ni has been studied by different investigators. In nearly all of the published reports, the evident objective was practical utility (8-9, 11-14). Knowledge of the oxidation of metal cyanide species is inadequate. The published reports claim depletion of  $\text{CN}^-$  from the solution, but say little or nothing about residual  $\text{CN}^-$  in precipitated metal-containing products. The literature search revealed no fundamental systematic kinetic and mechanism studies of oxidative metal-cyanide destruction reactions. A knowledge of the mechanisms of these reactions is needed to achieve a sufficient understanding of the fate of metal cyanide species in the environment and to design more effective cyanide destruction technology.

#### Possible Formation of Fulminates

Strong cyanide complexes, e.g., of Hg, Ag, and Au, may possibly react with strong oxidants by attack on the nitrogen atom of the CN group, with formation of fulminate ( $\text{CNO}^-$ ) complexes. In such strong cyanide complexes, the carbon atom, being strongly bonded to the metal ion, is not readily accessible to attack. An estimated value of the standard Gibbs energy of formation of  $\text{CNO}^-$  (table B-1), combined with the value for  $\text{CN}^-$ , yields an estimated standard reduction potential of  $E^\circ = +0.45 \text{ V}$  for the half-reaction



The value of  $E^\circ$  for this half-reaction allows the possibility that strong oxidants such as  $\text{ClO}^-$  or  $\text{O}_3$  may oxidize metal cyanide species to the metal fulminate species:

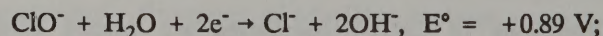




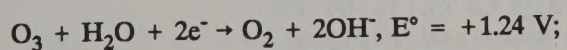
Table 8-4.-Nonoxidative decomposition of metal cyanide species

Metal	Reagent in dilute aqueous solution				Classification
	H <sub>2</sub> SO <sub>4</sub>	HCl	Na <sub>2</sub> S	H <sub>2</sub> S	
Zn(II)	Zn <sup>2+</sup>	Zn <sup>2+</sup>	ZnS	ZnS	WAD
Cd(II)	Cd <sup>2+</sup>	Cd <sup>2+</sup>	CdS	CdS	WAD
Hg(II)	Hg(CN) <sub>2</sub>	<sup>1</sup> HgCl <sub>2</sub>	HgS	HgS	part-WAD
Cu(I)	CuCN(s)	CuCN(s)	NR	Cu <sub>2</sub> S	part-WAD
Ag(I)	AgCN(s)	AgCl(s)	Ag <sub>2</sub> S	Ag <sub>2</sub> S	part-WAD
Au(I)	AuCN(s)	AuCN(s)	NR	NR	part-WAD
Ni(II)	Ni <sup>2+</sup>	Ni <sup>2+</sup>	NR	NiS	WAD
Co(III)	NR	NR	NR	NR	non-WAD
Fe(II)	NR	NR	NR	NR	non-WAD
Fe(III)	NR	NR	( <sup>2</sup> )	( <sup>2</sup> )	non-WAD
Mn(II)	Mn <sup>2+</sup>	Mn <sup>2+</sup>	MnS	MnS	WAD
Mn(III)	<sup>3</sup> Mn <sup>2+</sup>	<sup>3</sup> Mn <sup>2+</sup>	MnS	MnS	WAD
Cr(III)	Cr <sup>3+</sup>	Cr <sup>3+</sup>	NR	NR	WAD

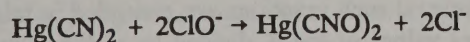
NR No reaction.

<sup>1</sup>Reaction may be incomplete.<sup>2</sup>[Fe(CN)<sub>6</sub>]<sup>3-</sup> reduced to [Fe(CN)<sub>6</sub>]<sup>4-</sup>.<sup>3</sup>C<sub>2</sub>N<sub>2</sub> also formed.

Note.—Cu(II) is not included because it is reduced rapidly to Cu(I) by CN<sup>-</sup>. Co(II) is not included because it is oxidized rapidly to Co(III) by O<sub>2</sub> in the presence of CN<sup>-</sup>.



from data in table B-1. This creates the possibility of explosive reaction products, especially if the solutions become concentrated, e.g.,



None of the publications concerning the oxidation of metal cyanide species consider the possible formation of fulminates, so this matter deserves investigation.

### CEMENTATION OF METALS FROM CYANIDE SOLUTIONS

The cementation of metals is often a suitable technique for removing metals from cyanide solutions. The best-known instance is the Merrill-Crowe process, in which

zinc dust is used to cement gold and silver from de-aerated cyanide pregnant solutions. Mercury, if present in such solutions, is also cemented. Table 8-6 lists standard reduction potentials for metal cyanide species. It shows that zinc could in theory also cement Cd, Cu, Ni, and Co from cyanide solutions. The reduction potentials are very negative, so that exclusion of O<sub>2</sub> may be required. The kinetically very inert [Co(CN)<sub>6</sub>]<sup>3-</sup> and [Fe(CN)<sub>6</sub>]<sup>4-</sup> may not react with metallic zinc.

Cementation with zinc would convert the partially WAD cyanide complexes of Hg, Cu, and Ag to metallic Hg, Cu, and Ag and the WAD zinc cyanide species. The latter are more readily destroyed with oxidants or treated with Na<sub>2</sub>S to remove zinc as ZnS and regenerate NaCN.

Cementation of mercury and silver from cyanide solutions with copper and subsequent destruction of the copper cyanide species with H<sub>2</sub>O<sub>2</sub> was reported (14).



Table 8-5.-Oxidative decomposition of metal cyanide species

Metal	Reagent in dilute alkaline solution			
	NaClO	<sup>1</sup> H <sub>2</sub> O <sub>2</sub>	O <sub>3</sub>	<sup>1</sup> HOOSO <sub>3</sub> <sup>-</sup>
Zn(II)	Zn(OH) <sub>2</sub>	Zn(OH) <sub>2</sub>	Zn(OH) <sub>2</sub>	Zn(OH) <sub>2</sub>
Cd(II)	Cd(OH) <sub>2</sub>	Cd(OH) <sub>2</sub>	Cd(OH) <sub>2</sub>	Cd(OH) <sub>2</sub>
Hg(II)	HgO?	HgO?	HgO?	HgO?
Cu(I)	Cu(OH) <sub>2</sub>	Cu(OH) <sub>2</sub>	Cu(OH) <sub>2</sub>	Cu(OH) <sub>2</sub>
Ag(I)	AgCl?	AgO <sub>x</sub> ?	AgO <sub>x</sub> ?	AgO <sub>x</sub> ?
Au(I)	AuCN?	AuCN?	AuCN	AuCN?
Ni(II)	NiO <sub>x</sub>	NiO <sub>x</sub> ?	NiO <sub>x</sub>	NiO <sub>x</sub>
Co(III)	NR	NR	NR	NR
Fe(II)	( <sup>2</sup> )	NR	( <sup>2</sup> )	( <sup>2</sup> )
Fe(III)	NR	( <sup>3</sup> )	NR	NR
Mn(II)	MnO <sub>x</sub> ? <sup>4</sup>	MnO <sub>x</sub> ? <sup>4</sup>	MnO <sub>x</sub> ? <sup>4</sup>	MnO <sub>x</sub> ? <sup>4</sup>
Mn(III)	MnO <sub>x</sub> ?	MnO <sub>x</sub> ?	MnO <sub>x</sub> ?	MnO <sub>x</sub> ?
Cr(III)	CrO <sub>4</sub> <sup>2-</sup> ?	CrO <sub>4</sub> <sup>2-</sup> ?	CrO <sub>4</sub> <sup>2-</sup> ?	CrO <sub>4</sub> <sup>2-</sup> ?

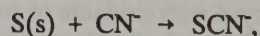
NR No reaction.

<sup>1</sup>With Cu catalyst.<sup>2</sup>[Fe(CN)<sub>6</sub>]<sup>4-</sup> oxidized to [Fe(CN)<sub>6</sub>]<sup>3-</sup>.<sup>3</sup>[Fe(CN)<sub>6</sub>]<sup>3-</sup> reduced to [Fe(CN)<sub>6</sub>]<sup>4-</sup>.<sup>4</sup>Probably via [Mn(CN)<sub>6</sub>]<sup>3-</sup>.

Note.—Question marks after entries denote uncertainty about expected products or rates of reaction. Cu(II) is not included because it is reduced rapidly to Cu(I) by CN<sup>-</sup>. Co(II) is not included because it is oxidized rapidly to Co(III) by O<sub>2</sub> in the presence of CN<sup>-</sup>.)

### REACTION OF METAL CYANIDE SPECIES WITH SULFUR OR POLYSULFIDES

The reactions of metal cyanide species with sulfur or polysulfides to form metal sulfides and SCN<sup>-</sup> provide an alternative route to the decomposition of metal cyanide species. The reactions of free CN<sup>-</sup> with sulfur and polysulfides are discussed in chapter 7. For the reaction



log K = 14.0 from standard Gibbs energy data in tables B-1 and C-1. This value of log K is sufficiently high that S(s)

or polysulfide ions S<sub>p</sub><sup>2-</sup> (p = 2 to 6) should react with metal cyanide species to form the metal sulfide and SCN<sup>-</sup>. Data for several such reactions are compiled in table 8-7, which gives values of log K divided by n, the number of CN<sup>-</sup> on the left side of the equation or of SCN<sup>-</sup> on the right side. The values of (log K)/n range from 10.2 to 22.9, so all of the reactions are thermodynamically capable of proceeding to completion. For the kinetically inert cobalt and iron cyanide complexes, the reactions with polysulfide ions or sulfur are not expected to proceed at an observable rate except possibly by photochemical action. The reaction of [Ni(CN)<sub>4</sub>]<sup>2-</sup> with polysulfide (32) to form a Ni(II) polysulfide complex was mentioned above.



Table 8-6.--Standard reduction potentials of metal cyanide species at 25° C

(Values are calculated from data in tables in appendix D)

Half-reaction (X = CN)	E°
$\text{ZnX}_4^{2-} + 2\text{e}^- \rightarrow \text{Zn(s)} + 4\text{X}^-$	-1.34
$\text{CdX}_4^{2-} + 2\text{e}^- \rightarrow \text{Cd(s)} + 4\text{X}^-$	- .93
$\text{HgX}_2 + 2\text{e}^- \rightarrow \text{Hg(l)} + 2\text{X}^-$	- .12
$\text{HgX}_4^{2-} + 2\text{e}^- \rightarrow \text{Hg(l)} + 4\text{X}^-$	- .30
$\text{CuX(s)} + \text{e}^- \rightarrow \text{Cu(s)} + \text{X}^-$	- .65
$\text{CuX}_3^{2-} + \text{e}^- \rightarrow \text{Cu(s)} + 3\text{X}^-$	-1.09
$\text{CuX}_4^{3-} + \text{e}^- \rightarrow \text{Cu(s)} + 4\text{X}^-$	-1.18
$\text{CuX}_4^{2-} + \text{e}^- \rightarrow \text{CuX}_4^{3-}$	+ .54
$\text{AgX(s)} + \text{e}^- \rightarrow \text{Ag(s)} + \text{X}^-$	- .13
$\text{AgX}_2^- + \text{e}^- \rightarrow \text{Ag(s)} + 2\text{X}^-$	- .41
$\text{AuX}_2^- + \text{e}^- \rightarrow \text{Au(s)} + 2\text{X}^-$	- .49
$\text{AuX}_4^- + 2\text{e}^- \rightarrow \text{AuX}_2^- + 2\text{X}^-$	+ .10
$\text{NiX}_4^- + 2\text{e}^- \rightarrow \text{Ni(s)} + 4\text{X}^-$	-1.12
$\text{CoX}_5^{3-} + 2\text{e}^- \rightarrow \text{Co(s)} + 5\text{X}^-$	- .97
$\text{CoX}_6^{3-} + \text{e}^- \rightarrow \text{CoX}_5^{3-} + \text{X}^-$	-1.08
$\text{FeX}_6^{4-} + 2\text{e}^- \rightarrow \text{Fe(s)} + 6\text{X}^-$	-1.52
$\text{FeX}_6^{3-} + \text{e}^- \rightarrow \text{FeX}_6^{4-}$	+ .36
$\text{MnX}_6^{4-} + 2\text{e}^- \rightarrow \text{Mn(s)} + 6\text{X}^-$	-1.49
$\text{MnX}_6^{3-} + \text{e}^- \rightarrow \text{MnX}_6^{4-}$	+ .07
$\text{MnX}_6^{2-} + \text{e}^- \rightarrow \text{MnX}_6^{3-}$	+1.52
$\text{CrX}_6^{4-} + 2\text{e}^- \rightarrow \text{Cr(s)} + 6\text{X}^-$	-1.45
$\text{CrX}_6^{3-} + \text{e}^- \rightarrow \text{CrX}_6^{4-}$	-1.39
$\text{TlX}_2^+ + 2\text{e}^- \rightarrow \text{Tl}^+ + 2\text{X}^-$	+ .35
$\text{TlX}_4^- + 2\text{e}^- \rightarrow \text{Tl}^+ + 4\text{X}^-$	+ .09

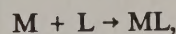
Polysulfide complexes of many metals have been reported recently, but in no other case was a metal cyanide species used in the preparation.

## OCCURRENCE OF OTHER METAL COMPLEXES IN CYANIDE PROCESS SOLUTIONS

Accessory species that may act as ligands and form complexes with metal ions exist in cyanide solutions. If the solutions contain metals in excess of the available  $\text{CN}^-$ , e.g., when oxidants are added to destroy  $\text{CN}^-$ , metal ions remaining in solution may be complexed by accessory species or  $\text{OH}^-$ . Important accessory species likely to occur in cyanide solutions are as follows, classified by source:

- Hydrolysis or oxidation of  $\text{CN}^-$ :  $\text{NH}_3$ ,  $\text{SCN}^-$ .
- Minerals:  $\text{SH}^-$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ .
- Reagents:  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ .

As described in chapter 4, if the concentration of a free ligand in a solution of a metal ion exceeds a certain value, the metal ion will exist predominantly in the form of complexes with that ligand. Simply, in a reaction



for which the equilibrium constant is

$$K = [\text{ML}]/[\text{M}][\text{L}],$$

the concentration  $[\text{L}]_{\min}$  of free ligand L above which the predominant metal species will be the complex ML is given by

$$\text{pL}_{\min} = -\log [\text{L}]_{\min} = \log K.$$

Values of  $\text{pL}_{\min}$  for the ligands listed above with different metal ions are compiled in table 8-8. The values in table 8-8 are all relative to unhydrolyzed metal ions, so at pH values at which the metal ions are hydrolyzed, higher ligand concentrations are required to compete with  $\text{OH}^-$  and form complexes. Consequently, the values in table 8-8 are conservative when applied to alkaline solutions, but can still be used to indicate the possibility of the predominance of soluble metal complexes with accessory ligands. For a simple example, consider a solution depleted in  $\text{CN}^-$  contains trace heavy metals and  $1 \times 10^{-5}M$   $\text{S}_2\text{O}_3^{2-}$ , i.e.,  $\text{L} = \text{S}_2\text{O}_3^{2-}$ , and  $\text{pL} = -\log [\text{L}] = 5.0$ . Table 8-8 shows that  $\text{Hg}^{2+}$ ,  $\text{Cu}^+$ ,  $\text{Ag}^+$ , and  $\text{Au}^+$  have  $\text{pL}_{\min}$  for  $\text{S}_2\text{O}_3^{2-}$  complexes above 5.0, and  $\text{S}_2\text{O}_3^{2-}$  complexes would predominate except at high pH values where  $\text{OH}^-$  would compete with  $\text{S}_2\text{O}_3^{2-}$ .



Table 8-7.-Reactions of free cyanide and metal cyanide species with polysulfide ions or sulfur

Reaction	(log K)/n <sup>1</sup>
$S(s) + CN^- \rightarrow SCN^-$	14.0
$Zn(CN)_2(s) + S_3^{2-} \rightarrow ZnS(s) + 2SCN^-$	17.6
$[Zn(CN)_4]^{2-} + S_5^{2-} \rightarrow ZnS(s) + 4SCN^-$	14.3
$Cd(CN)_2 + S_3^{2-} \rightarrow CdS(s) + 2SCN^-$	21.2
$[Cd(CN)_4]^{2-} + S_5^{2-} \rightarrow CdS(s) + 4SCN^-$	15.4
$Hg(CN)_2 + S_3^{2-} \rightarrow HgS(s) + 2SCN^-$	22.9
$[Hg(CN)_4]^{2-} + S_5^{2-} \rightarrow HgS(s) + 4SCN^-$	16.4
$2CuCN(s) + S_3^{2-} \rightarrow Cu_2S(s) + 2SCN^-$	16.9
$2[Cu(CN)_2]^- + S_5^{2-} \rightarrow Cu_2S(s) + 4SCN^-$	13.8
$2[Cu(CN)_3]^{2-} + S_5^{2-} + 2S(s) \rightarrow Cu_2S(s) + 6SCN^-$	12.1
$2AgCN(s) + S_3^{2-} \rightarrow Ag_2S(s) + 2SCN^-$	22.0
$2[Ag(CN)_2]^- + S_5^{2-} \rightarrow Ag_2S(s) + 4SCN^-$	15.1
$2AuCN(s) + S_3^{2-} \rightarrow Au_2S(s) + 2SCN^-$	15.1
$2[Au(CN)_2]^- + S_5^{2-} \rightarrow Au_2S(s) + 4SCN^-$	11.5
$Ni(CN)_2(s) + S_3^{2-} \rightarrow NiS(s) + 2SCN^-$	15.0
$[Ni(CN)_4]^{2-} + S_5^{2-} \rightarrow NiS(s) + 4SCN^-$	11.3
$[Co(CN)_6]^{3-} + (1/2)S_4^{2-} + S_5^{2-} \rightarrow CoS(s) + 6SCN^-$	11.2
$[Fe(CN)_6]^{4-} + S_5^{2-} + 2S(s) \rightarrow FeS(s) + 6SCN^-$	10.2
$[Fe(CN)_6]^{3-} + (1/2)S_4^{2-} + S_5^{2-} \rightarrow FeS(s) + 6SCN^-$	12.3

<sup>1</sup>Calculated from data in tables B-1, C-1, and most of the tables in appendix D; n is the number of CN<sup>-</sup> groups on the left side of the equation or of SCN<sup>-</sup> ions on the right.



Table 8-8.--Minimum free ligand concentrations required predominance of soluble metal complexes with the ligand

Metal ion	pL of specified ligand L (pH range)						
	CN <sup>-</sup> >9	Cl <sup>-</sup> >0	SH <sup>-</sup> >7	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> >2	SO <sub>4</sub> <sup>2-</sup> >2	NH <sub>3</sub> >9	SCN <sup>-</sup> >0
Zn <sup>2+</sup>	5.6	0.5	(7)	2.4	2.3	2.4	1.3
Cd <sup>2+</sup>	6.0	2.0	(8)	3.9	2.5	2.5	1.9
Hg <sup>2+</sup>	17.0	6.8	(19)	(15)	2.7	(9.0)	9.2
Cu <sup>+</sup>	10.8	2.8	(14)	(11)	(1)	(5.8)	(6)
Cu <sup>2+</sup>	R	.2	R	R	2.3	4.0	2.3
Ag <sup>+</sup>	10.2	3.3	(16)	8.7	1.3	3.6	4.8
Au <sup>+</sup>	(19)	(4.6)	(20)	(18)	(1)	(10)	(8.8)
Au <sup>3+</sup>	(20)	>7	R	R	(4)	>16	>11
Ni <sup>2+</sup>	7.6	(.3)	N	(2)	2.3	2.7	1.8
Co <sup>2+</sup>	(4.6)	(.3)	N	(2)	2.3	2.0	1.7
Co <sup>3+</sup>	(12.2)	(2.1)	R	R	(4.0)	(>6)	R
Fe <sup>2+</sup>	5.9	(.2)	N	(2)	2.3	1.4	1.3
Fe <sup>3+</sup>	7.0	1.5	R	(4)	4.0	N	3.0
Mn <sup>2+</sup>	(1.7)	(.1)	N	(2)	2.3	.9	1.2
Mn <sup>3+</sup>	(5.8)	(1.8)	R	R	(4.0)	N	R
Cr <sup>3+</sup>	(5.5)	(.5)	N	(4)	(4.0)	(>2)	3.1

N No data.

R Redox reaction.

Note.—All data are for 25° C and ionic strength zero, and are derived from the tables in appendix D. Data are expressed as pL = -log[L], where [L] is the free ligand concentration. The approximate pH range in which the specified ligand species L is the predominant form of the free ligand is specified. Values in parentheses are estimated.



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<sup>2</sup>A title in parentheses is a translation from the language in which the work was published.



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## CHAPTER 9.—PHOTOCHEMISTRY OF METAL CYANIDE SPECIES

### INTRODUCTION

Sunlight plays an important role in environmental chemistry by initiating photochemical reactions. Sunlight is therefore an important contributor to the degradation of pollutants, including cyanides. The cyanide complexes of certain metals, namely Co, Fe, and Cr, are not rapidly decomposed by acids or destroyed by oxidants. However, the cyanide complexes of Co, Fe, and Cr undergo photochemical decomposition when irradiated with blue to near-ultraviolet light, 500 to 300 nm wavelength. Solar ultraviolet light encompasses this wavelength range and will cause photochemical decomposition of these metal cyanide complexes.

This chapter begins with a review of the principles of photochemistry, followed by presentation of photochemical information on the cyanide complexes of Co, Fe, and Cr. The chapter concludes with a brief review of the oxidation of free  $\text{CN}^-$  by  $\text{O}_2$  photocatalyzed by  $\text{TiO}_2$ .

### PRINCIPLES OF PHOTOCHEMISTRY

A treatise on the photochemistry of metal compounds (1) provides background information. At ambient temperatures, practically all chemical species are in their lowest energy electronic state, termed the "electronic ground state." States at higher electronic energy levels are termed "electronically excited states." A chemical species must absorb light energy to be raised from its ground state to an electronically excited state.

Photochemical reactions are chemical reactions undergone by a chemical species in an electronically excited state. To distinguish photochemical reactions from reactions of chemical species in their electronic ground states, the latter are termed "thermal reactions." Photochemical reactions are particularly important for chemical species that undergo slow thermal reactions. The products obtained in photochemical reactions are often different from the products obtained in thermal reactions. The yield of a product in a photochemical reaction is defined as the number of moles of product formed per mole of photons absorbed by the substrate, and is termed the "quantum efficiency" or "quantum yield." By definition, the maximum value of the quantum yield is 1, unless a chain reaction occurs, in which case quantum yields higher than 1 may be observed. Quantum yields depend on the chemical properties of the species in its electronically excited states and not on the molar absorptivity.

The energy content of a mole of photons is given by

$$E = N^{\circ}hc/L = (1,20 \times 10^8)/L \quad (9-1)$$

where  $N^{\circ}$  = Avogadro's number,  $6.02 \times 10^{23} \text{ mol}^{-1}$ ,

$h$  = Planck's constant,  $6.63 \times 10^{-34} \text{ J} \cdot \text{s}$ ,

$c$  = velocity of light,  $2.998 \times 10^8 \text{ m} \cdot \text{s}^{-1}$ ,

and  $L$  = wavelength of light ( $\lambda$ ).<sup>1</sup> For violet light of wavelength 400 nm, equation 9-1 gives  $E = 299 \text{ kJ} \cdot \text{mol}^{-1}$ .

The accuracy of experimental determination of quantum yields varies from 10 to 50 pct, depending on the magnitude of the quantum yield, the molar absorptivity at the wavelength employed, and the complexity of the system being investigated. The magnitudes of quantum yields depend on the nature of the electronically excited states, which determines what photochemical reactions will occur. Different bands in the absorption spectrum correspond to excitation to different electronically excited states. Consequently, the observed photochemical reactions and quantum yields vary with the wavelength of the absorbed light. Within the wavelength range of a single absorption band, the same photochemical reactions usually occur, and the quantum yield often does not vary greatly.

Often the product of a photochemical reaction absorbs light and may undergo further photochemical reactions. The extent to which this occurs may cause experimental difficulties in quantum yield determinations. Consequently, determination of the quantum yield for the first photochemical reaction in an irradiated system can be challenging. There are many examples, such as the hexacyanoferrates, for which there is much disagreement in published quantum yields.

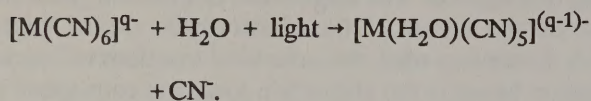
Photochemical reactions also occur indirectly in the form of photosensitized reactions. In photosensitized reactions, an accessory solution species, the photosensitizer, absorbs light and is raised to an excited electronic state. The excited photosensitizer then transfers the energy of its electronic excited state to another species, the substrate, and raises it to an excited electronic state, and the excited substrate undergoes reactions. The energy of the electronic excited state of the photosensitizer must be greater than the energy of the electronic excited state of the substrate. Hence, the photosensitizer must absorb light at a shorter wavelength (higher energy) than the substrate. The excited electronic state of the substrate generated in a photosensitization may be different from the excited electronic states obtained when the substrate absorbs light directly; consequently, different photochemical reactions may occur.

<sup>1</sup>Italic numbers in parentheses refer to items in the list of references at the end of this chapter.



Photochemical reaction products may be thermodynamically unstable with respect to the ground-state substrate or its thermal reaction products. If the requisite equilibria are not rapidly established, the photochemical reaction products can be isolated and characterized. The cyanide complexes of Co, Fe, and Cr are characterized by slow thermal reactions. The cyanide complexes of these metals undergo photochemical reactions with formation of reaction products that are thermodynamically unstable with respect to the ground-state substrates. However, those products are relatively unreactive and can be isolated and characterized.

For the hexacyanometallates of Co(III), Fe(II), Fe(III), and Cr(III), the initial photochemical reaction observed in near-ultraviolet irradiation is substitution of one CN<sup>-</sup> by H<sub>2</sub>O:



The aquopentacyanometallate product is thermodynamically unstable with respect to reacting with CN<sup>-</sup> to reform the hexacyanometallate, but the rate of this reaction is relatively slow. If the photochemical decomposition is conducted at pH below 9, the liberated CN<sup>-</sup> is converted to HCN and can be easily removed to prevent the reverse of this photochemical reaction. The aquopentacyanometallate product then undergoes other reactions.

Most of the remainder of this chapter reviews the photochemistry of the cyanide complexes of these four metal ions. Sharpe's monograph (2) is the major source of data, but a number of more recent or otherwise important references were also consulted (3-36). Table 5-2 may be consulted to correlate the absorption spectral data with the photochemical data.

## COBALT

Near-ultraviolet irradiation of hexacyanocobaltate(III) [Co(CN)<sub>6</sub>]<sup>3-</sup> results initially in aquation with loss of 1 mol CN<sup>-</sup> per mole cobalt and formation of [Co(H<sub>2</sub>O)(CN)<sub>5</sub>]<sup>2-</sup>. The latter is a weak acid and forms [Co(OH)(CN)<sub>5</sub>]<sup>3-</sup> at pH above about 10. The quantum efficiency of this photochemical reaction at pH 2 to 7 is 0.31, independent of wavelength from 254 to 365 nm (3). Further ultraviolet irradiation results in loss of more CN<sup>-</sup>, with formation of [Co(H<sub>2</sub>O)<sub>2</sub>(CN)<sub>4</sub>]<sup>-</sup> and [Co(H<sub>2</sub>O)<sub>3</sub>(CN)<sub>3</sub>] or the hydroxo species formed by dissociation of H<sup>+</sup> from them (4-6). Continued irradiation is said to result in conversion to cobalt oxides, but no data are given (5-6).

Regarding photosensitized aquation of [Co(CN)<sub>6</sub>]<sup>3-</sup>, only one publication on photosensitization by biacetyl, H<sub>3</sub>C-CO-CO-CH<sub>3</sub>, was located (7).

Photochemically assisted destructive oxidation of [Co(CN)<sub>6</sub>]<sup>3-</sup> by O<sub>3</sub> has been reported; no details were given (8).

## IRON

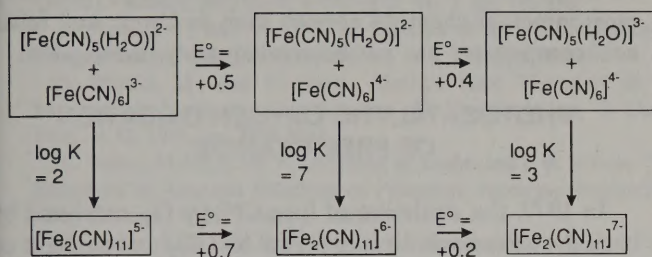
Near-ultraviolet irradiation of [Fe(CN)<sub>6</sub>]<sup>4-</sup> results initially in loss of 1 mol CN<sup>-</sup> per mole iron and formation of [Fe(CN)<sub>5</sub>(H<sub>2</sub>O)]<sup>3-</sup>. Reported values of the quantum efficiency vary widely. This was attributed to inadequate experimental techniques and the complexity of the system, which was not realized by many earlier investigators (9). The quantum yield is the same at 313 and 365 nm and is constant at pH 4 to 10 (10). The quantum yield was redetermined at 365 nm and is 0.9 at pH 5 to 11, but drops steadily to 0.5 at pH 1 (9). The lower values in acid solution were attributed to formation of [HFe(CN)<sub>6</sub>]<sup>3-</sup> and [H<sub>2</sub>Fe(CN)<sub>6</sub>]<sup>2-</sup>. The initial product [Fe(CN)<sub>5</sub>(H<sub>2</sub>O)]<sup>3-</sup> is also photosensitive, but no quantum yield data were located. Intermediates such as [Fe(CN)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2-</sup> have not been characterized in aqueous solution at any pH. Continued near-ultraviolet irradiation leads to complete decomposition to Fe<sup>2+</sup> and HCN in acid solution in the absence of O<sub>2</sub>; a precipitate of prussian blue forms in the presence of O<sub>2</sub>. In alkaline solution in the presence of O<sub>2</sub>, [Fe(CN)<sub>5</sub>(H<sub>2</sub>O)]<sup>3-</sup> is oxidized to [Fe(CN)<sub>5</sub>(OH)]<sup>3-</sup>, and continued irradiation results in conversion to Fe(III) oxide products with liberation of free CN<sup>-</sup>/HCN, which may be oxidized to an unknown extent.

Irradiation of [Fe(CN)<sub>6</sub>]<sup>3-</sup> with blue to near-ultraviolet light results initially in loss of 1 mol CN<sup>-</sup> per mole iron and formation of [Fe(CN)<sub>5</sub>(H<sub>2</sub>O)]<sup>2-</sup>. The latter species is a weak acid and forms [Fe(CN)<sub>5</sub>(OH)]<sup>3-</sup> at pH above about 8. As is the case for the Fe(II) system, reported values of the quantum efficiency vary widely, and this may be attributed to inadequate experimental techniques in view of the complexity of the system (11). The quantum efficiency of the reaction is low and independent of pH. The quantum efficiency was redetermined at pH 11 to be 0.04 at 254 nm and 0.016 at 366 nm (11). The initial product [Fe(CN)<sub>5</sub>(H<sub>2</sub>O)]<sup>2-</sup> or [Fe(CN)<sub>5</sub>(OH)]<sup>3-</sup> is also photosensitive. The quantum yield for loss of 1 mol CN<sup>-</sup> per mole iron from [Fe(CN)<sub>5</sub>(H<sub>2</sub>O)]<sup>2-</sup> at pH 7 is about 0.015 at 365 nm (12). Intermediates such as [Fe(H<sub>2</sub>O)<sub>2</sub>(CN)<sub>4</sub>]<sup>-</sup> have not been characterized in aqueous solution at any pH. Continued irradiation results in formation of prussian blue in acid solution or Fe(III) oxides in alkaline solution, with liberation of free CN<sup>-</sup>/HCN, which may be oxidized to an unknown extent.

The information in the preceding two paragraphs is summarized in figure 9-1. Figure 9-1 also shows pertinent thermal reactions, such as oxidation by O<sub>2</sub> which are described in chapter 8. With both [Fe(CN)<sub>6</sub>]<sup>4-</sup> and [Fe(CN)<sub>6</sub>]<sup>3-</sup> in the presence of air, the ultimate product is



Figure 9-1



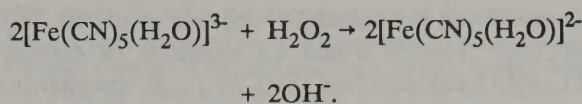
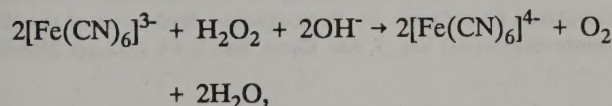
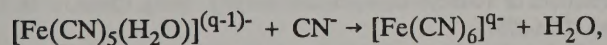
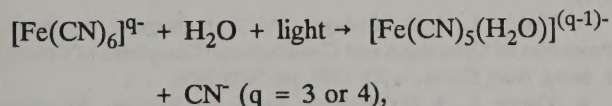
### Photochemical decomposition of hexacyanoferrates.

prussian blue in acid solutions and  $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$  in alkaline solutions.

As noted above, many photochemical studies of iron cyanide species seriously disagree, e.g., in regard to published quantum yields. The disagreements have been attributed to use of nonmonochromatic light, spectrophotometric observations at only one wavelength, failure to prevent oxidation of Fe(II) species by  $\text{O}_2$ , competing photochemical reactions of initial products, interfering reactions of analytical reagents, failure to recognize condensation reactions that form dinuclear species (see chapter 8), and the instability of  $\text{Na}_3[\text{Fe}(\text{CN})_5(\text{H}_2\text{O})]$  used as a reagent (9, 13).

Broderius (14) published extensive calculations of the photochemical decomposition rates of  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$  as a function of solar illumination versus latitude and time of year. His values of molar absorptivity for both complexes are about 5 pct higher than the values given in table 5-2. He determined the respective quantum yields in sunlight as 0.14 and 0.0023, which are based on liberated  $\text{CN}^-/\text{HCN}$  in the presence of air. These values are much lower than the values given above for the photochemical elimination of 1 mol  $\text{CN}^-$  per mole iron from  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$ , which shows that further photochemical degradation of the initially produced aquopentacyanoferrates is relatively less efficient.

The near-ultraviolet irradiation of  $[\text{Fe}(\text{CN})_6]^{4-}$  or  $[\text{Fe}(\text{CN})_6]^{3-}$  in alkaline solution in the presence of  $\text{H}_2\text{O}_2$  results in photocatalytic decomposition of the  $\text{H}_2\text{O}_2$  (15-16):



The initial photochemical reaction products  $[\text{Fe}(\text{CN})_5(\text{H}_2\text{O})]^{(q-1)-}$  undergo thermal condensation reactions with water elimination, with themselves or with  $[\text{Fe}(\text{CN})_6]^{q-}$ , to form  $[\text{Fe}(\text{CN})_{102}(\text{H}_2\text{O})]^x$ ,  $[\text{Fe}_2(\text{CN})_{10}]^x$ , and  $[\text{Fe}_2(\text{CN})_{11}]^x$ , as described in chapter 8. All of these species and their redox and photochemical reactions make the environmental chemistry of iron cyanide species quite complex. As also stated in chapters 5 and 8, many of these iron cyanide species require improved characterization with regard to their visible and ultraviolet absorption spectra and their thermal chemical and photochemical reactions.

The fate of  $\text{CN}^-$  liberated during photochemical decomposition of  $[\text{Fe}(\text{CN})_6]^{q-}$  is unknown. In alkaline photodecomposition of  $[\text{Fe}(\text{CN})_6]^{3-}$ ,  $\text{CN}^-$  was reported to be oxidized to  $\text{NCO}^-$  (17-18), but detailed data were not available. It is possible that the presence of Fe(III) species or  $\text{O}_2$  leads to oxidation of  $\text{CN}^-$  to  $\text{NCO}^-$  in alkaline solutions or to  $\text{C}_2\text{N}_2$  or  $\text{HNCO}$  in acid solution. The  $[\text{Fe}(\text{CN})_6]^{3-}$  and other Fe(III) species oxidize  $\text{CN}^{3-}$  to  $\text{NCO}^-$  in alkaline solution in the presence of catalytically active copper species (see chapter 8). The role of light and the possibility of catalysis by iron oxides, other iron species, other copper species, or other agents such as clays or carbonaceous materials are unknown.

No literature was located regarding photosensitized decomposition of iron cyanide complexes.

Ultraviolet irradiation in the presence of oxidants has been reported to destroy iron cyanide complexes (9, 19-20). With  $\text{O}_3$  as the oxidant, total  $\text{CN}^-$ ,  $7.6 \text{ mg} \cdot \text{L}^{-1}$  as  $[\text{Fe}(\text{CN})_6]^{4-}$  or  $[\text{Fe}(\text{CN})_6]^{3-}$ , decreased to  $0.3 \text{ mg} \cdot \text{L}^{-1}$  in 1 h (19). Another study with  $\text{ClO}_2$  as the oxidant was reported (20); the  $\text{ClO}_2$  is photodecomposed to reactive radicals that oxidize  $\text{CN}^-$ . Electrochemical oxidation of liberated  $\text{CN}^-$  has also been utilized (21). Another Japanese study with no oxidant specified was also reported (22-23).

Photocatalytic degradation of  $0.001M$   $[\text{Fe}(\text{CN})_6]^{3-}$  in sunlight-irradiated  $0.01M$   $\text{TiO}_2 \cdot x\text{H}_2\text{O}$  at pH 10 was recently claimed (24). The  $\text{TiO}_2 \cdot x\text{H}_2\text{O}$  suspension was prepared by addition of  $\text{TiCl}_4$  to water, and stabilized after alkali addition to pH 10 with polyvinyl alcohol. The disappearance of  $[\text{Fe}(\text{CN})_6]^{3-}$  was monitored by absorbance measurements at its 420-nm absorption maximum. The reaction products were assumed, not demonstrated, to be oxidation products of  $\text{CN}^-$ . The evidence does not necessarily support the claim that  $[\text{Fe}(\text{CN})_6]^{3-}$  was degraded. The molar absorptivity of  $[\text{Fe}(\text{CN})_6]^{4-}$  at 420 nm is lower than that of  $[\text{Fe}(\text{CN})_6]^{3-}$  by a factor of  $10^3$  (see chapter 5). Titanium(IV) and  $[\text{Fe}(\text{CN})_6]^{4-}$  react at pH 2 to form an



orange-colored precipitate (25-26), but at pH 10,  $\text{Ti(IV)-[Fe(CN)}_6\text{]}^{4-}$  species would be expected to convert to  $\text{TiO}_2 \cdot x\text{H}_2\text{O}$  and dissolved  $[\text{Fe(CN)}_6]^{4-}$ . If absorbance was monitored at 420 nm alone,  $[\text{Fe(CN)}_6]^{4-}$  or the orange  $\text{Ti(IV)-[Fe(CN)}_6\text{]}^{4-}$  species would not have been detected. Consequently, the observed disappearance of  $[\text{Fe(CN)}_6]^{3-}$  may have been caused simply by photocatalyzed reduction to  $[\text{Fe(CN)}_6]^{4-}$  and not by photocatalyzed oxidative degradation of  $[\text{Fe(CN)}_6]^{3-}$ .

## CHROMIUM

Near-ultraviolet irradiation of  $[\text{Cr(CN)}_6]^{3-}$  results initially in loss of 1 mol  $\text{CN}^-$  per mole chromium and formation of  $[\text{Cr(H}_2\text{O)}(\text{CN})_5]^{2-}$ . The latter species is a weak acid and forms  $[\text{Cr(OH)}(\text{CN})_5]^{3-}$  at pH above about 9. Marchaj and Stasicka (27) have reviewed the literature and reported their own observations; the quantum yield is 0.10 to 0.12 at pH 3 to 9 over the wavelength range 265 to 405 nm. Continued near-ultraviolet irradiation results in progressive elimination of more  $\text{CN}^-$  (27-28), and most of the intermediate species have been characterized as described in chapter 8. The final products are Cr(III) oxides in alkaline or neutral solutions and  $\text{Cr}^{3+}$  in acid solution. The quantum yield for loss of 1 mol  $\text{CN}^-$  per mole chromium from  $[\text{Cr(H}_2\text{O)}(\text{CN})_5]^{2-}$  at pH 6 is 0.04 at 436 nm; the quantum yield for loss of 1 mol  $\text{CN}^-$  per mole chromium from  $[\text{Cr(OH)}(\text{CN})_5]^{3-}$  at pH 14 is 0.06 at 313 nm and 0.09 at 436 nm (27).

Photosensitized decomposition of hexacyanochromate(III) by acridine, naphthalene, pyrazine, and xanthone has been reported (29).

No publications concerning photochemically assisted oxidative destruction of Cr(III) cyanide complexes were located except for the reported formation of  $\text{CrO}_4^{2-}$  during irradiation in the presence of  $\text{O}_2$  (28). A systematic investigation of this reaction was not conducted.

## SUMMARY OF PHOTOCHEMISTRY OF METAL CYANIDE COMPLEXES

The cyanide complexes of Co, Fe, and Cr undergo photochemical reactions in blue to ultraviolet light, i.e., wavelengths below 500 nm. Solar ultraviolet radiation down to 300 nm penetrates to the Earth's surface. The Co, Fe, and Cr cyanide complexes all absorb light in the 300- to 500-nm region, and they are subject to photochemical degradation by solar radiation. The ultimate metal-containing decomposition products in aerated alkaline solutions are metal oxides. The extent to which liberated  $\text{CN}^-$  is oxidized during environmental photochemical degradation of Co, Fe, and Cr cyanide complexes is not known.

The extent to which photosensitization influences the decomposition of metal cyanide complexes by accessory environmental chemical species such as humic and fulvic acid components has not been adequately investigated.

## PHOTOCATALYTIC OXYGEN OXIDATION OF FREE CYANIDE

In 1977, the oxidation of free  $\text{CN}^-$  by  $\text{O}_2$ , catalyzed by both the anatase and rutile forms of  $\text{TiO}_2$  and sunlight or artificial ultraviolet light, was reported (30-32). A solution of KCN initially 0.001M was 99 pct oxidized in 2 days of sunlight exposure in the presence of anatase. Cyanate was qualitatively identified as an oxidation product. Tests for other oxidation products apparently were not performed. Photocatalyzed oxidation of  $\text{CN}^-$  on ZnO and CdS was also reported (31), but ZnO and CdS were reported to degrade after extended use (32).

Other groups of investigators have subsequently investigated the photocatalyzed oxidation of  $\text{CN}^-$  on  $\text{TiO}_2$  (33-37). With anatase, the reaction was 6 times faster at pH 11 than at pH 14; if the anatase was platinized, the rate was 20 times faster than with untreated anatase at pH 11 (34).

Recently it was found that roasted ilmenite photocatalyzed the oxidation of  $\text{CN}^-$  by  $\text{O}_2$  with efficiency comparable to that of anatase (36). Anatase was observed to be more effective than rutile, but this difference was attributed to different specific surface areas (36).

The formation of  $\text{NCO}^-$  as an oxidation product in the photocatalyzed oxygen oxidation of  $\text{CN}^-$  was demonstrated (36). Further investigation showed that  $\text{NCO}^-$  was further photocatalytically oxidized on anatase to  $\text{NO}_2^-$  and  $\text{NO}_3^-$ .

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## CHAPTER 10.—MIXTURES OF METAL CYANIDE SPECIES

### INTRODUCTION

Cyanide process and waste solutions usually contain mixtures of cyanide species of different metals. This chapter addresses reactions between metal cyanide species and the cations and oxide species of different metals. These reactions are important under the following circumstances:

1. Insufficient  $\text{CN}^-$  is present to convert all cyanide-reactive metal species to anionic cyanide complexes. This situation occurs when oxidative removal of  $\text{CN}^-$  or natural degradation of cyanide species is incomplete.

2. Metal salts, such as  $\text{Fe(II)}$  salts, are intentionally added to precipitate cyanides. Iron(II) reacts with free  $\text{CN}^-$  and the  $\text{CN}^-$  in most weak-acid dissociable (WAD) cyanide species to form hexacyanoferrate (II)  $[\text{Fe}(\text{CN})_6]^{4-}$ , which is precipitated by excess  $\text{Fe(II)}$ ,  $\text{Fe(III)}$ , or other metal cations. This practice has been employed by some processors to rapidly and inexpensively mitigate the toxicity of cyanides. However, as discussed in this chapter, the reaction of cyanide complexes of  $\text{Hg}$ ,  $\text{Cu}$ ,  $\text{Ag}$ , and  $\text{Ni}$  with  $\text{Fe(II)}$  salts is incomplete. This behavior correlates with the partially WAD classification of the cyanide complexes of  $\text{Hg}$ ,  $\text{Cu}$ , and  $\text{Ag}$  discussed in chapter 8.

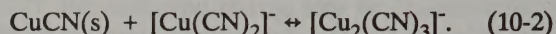
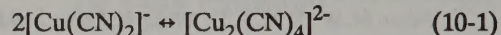
Sharpe's monograph (1)<sup>1</sup> is the major source of data on this subject. Other pertinent or more recent references are cited where appropriate.

### REACTIONS BETWEEN DISSOLVED METAL CYANIDE SPECIES

#### *Existence of Polynuclear Metal Cyanide Complexes of Individual Metals*

The published equilibrium data for cyanide species of  $\text{Zn(II)}$ ,  $\text{Cd(II)}$ ,  $\text{Hg(II)}$ ,  $\text{Cu(I)}$ ,  $\text{Ag(I)}$ , and  $\text{Ni(II)}$  (appendix D) were obtained at metal concentrations below  $0.01M$  and show no evidence of formation of polynuclear species. Formation of polynuclear species would be favored by high metal concentrations,  $>0.01M$ , and low  $\text{CN}^-$ -metal mole ratios,  $\text{CN}^-$ -metal  $<3$ . In the  $\text{Zn(II)}$ ,  $\text{Cu(I)}$ ,  $\text{Ag(I)}$ , and  $\text{Ni(II)}$  systems, the low solubility of  $\text{Zn}(\text{CN})_2$ ,  $\text{CuCN}$ ,  $\text{AgCN}$ , and  $\text{Ni}(\text{CN})_2$ , respectively, opposes the formation of polynuclear species, except possibly in concentrated solutions of the anionic complexes. In the case of  $\text{Cu(I)}$ ,

salts such as  $\text{KCu}_2(\text{CN})_3$  are known; in concentrated solutions, with  $\text{Cu(I)} > 0.1M$ , equilibria involving polynuclear species may exist:



Reaction 10-2 implies a higher solubility of  $\text{CuCN}$  in concentrated  $\text{Cu(I)-CN}^-$  solutions than indicated by known equilibrium data.

In the  $\text{Hg(II)-CN}^-$  system,  $\text{Hg}(\text{CN})_2$  is soluble, and there is evidence for polynuclear cyanide species in solutions of  $\text{Hg}(\text{CN})_2$  and  $\text{Hg(II)}$  salts such as  $\text{Hg}(\text{ClO}_4)_2$ , e.g.,  $[\text{Hg}_2(\text{CN})_2]^{2+}$  (see table D-5). The soluble  $\text{Cd}(\text{CN})_2$  may also form polynuclear complexes, but investigations of solutions of sufficiently high concentration have not been published.

Dinuclear iron cyanide complexes are formed by condensation reactions involving the photochemically generated pentacyanoferrates, as described in chapters 8 and 9. They are all unstable with respect to decomposition to hexacyanoferrates and insoluble iron cyanides. Dinuclear cyanide complexes are known for  $\text{Co(II)}$  and  $\text{Mn(III)}$ , and are likely for  $\text{Co(III)}$  and  $\text{Cr(III)}$ , as discussed in chapter 8.

In summary, polynuclear metal cyanide complexes are not expected to exist to a significant extent in mineral-processing solutions, where metal concentrations rarely exceed  $10^{-2}M$ . A possible exception may be iron cyanide complexes formed via photochemical reactions.

#### *Existence of Polynuclear Cyanide Complexes in Mixtures of Different Metals*

The considerations raised in connection with polynuclear cyanide complexes in solutions containing a single metal apply also to solutions containing more than one metal. In metallurgical solutions, soluble mixed-metal polynuclear cyanide complexes such as  $[\text{CuAg}(\text{CN})_4]^{2-}$  are thus not expected to exist to a significant extent.

Complexes of the soluble  $\text{Hg}(\text{CN})_2$  with other metal species are known. The  $\text{Hg}(\text{CN})_2$  forms weak complexes ( $\log K$  about 2) with the hexacyanoferrates, e.g.  $[\text{Hg}(\text{CN})_2\text{Fe}(\text{CN})_6]^{4-}$ , and other cyanometallate anions. Some metal cations, e.g.,  $\text{Ag}^+$ , also form weak complexes with  $\text{Hg}(\text{CN})_2$ . In these complexes,  $\text{Hg}(\text{CN})_2$ , which has a linear molecular structure  $\text{NC-Hg-CN}$ , functions like an organic nitrile  $\text{R-CN}$ , where  $\text{R}$  is an alkyl or aryl group. It is possible that  $\text{Cd}(\text{CN})_2$  behaves similarly.

<sup>1</sup>Italic numbers in parentheses refer to items in the list of references at the end of this chapter.



## REACTIONS BETWEEN ANIONIC METAL CYANIDE SPECIES AND METAL CATIONS

### *Cyanide Species of Zinc, Cadmium, Mercury, Copper, Silver, and Nickel*

The anionic cyanide complexes of Zn(II), Cd(II), Hg(II), Cu(I), Ag(I), and Ni(II) give precipitates with many heavy-metal cations. Little is known about the details of those reactions.

In some cases, there is evidence that the precipitates contain the same species as the solutions from which they were formed, e.g.,  $\text{Zn}[\text{Ni}(\text{CN})_4] \cdot x\text{H}_2\text{O}$ . If the cation forms a stronger cyanide complex than the metal in the anionic cyanide complex initially present, the solid compound is subject to decomposition or rearrangement. For example, the yellow  $[\text{Ni}(\text{CN})_2]^{2-}$  is about 10 log K units stronger than the colorless  $[\text{Zn}(\text{CN})_4]^{2-}$ . Addition of a solution of a  $\text{Ni}^{2+}$  salt to a solution of  $[\text{Zn}(\text{CN})_4]^{2-}$  gives a light-green precipitate of  $\text{Ni}[\text{Zn}(\text{CN})_4] \cdot x\text{H}_2\text{O}$ , which rearranges to yellow  $\text{Zn}[\text{Ni}(\text{CN})_4] \cdot x\text{H}_2\text{O}$ .

In other cases, the obtained precipitates may be merely mixtures of the binary neutral cyanides of the component metals. With  $\text{Hg}(\text{CN})_4^{2-}$ , decomposition to soluble  $\text{Hg}(\text{CN})_2$ , free  $\text{CN}^-$ , and the cyanide of the other metal may occur.

No equilibrium data are available for any of the reactions just described. However, equilibrium data for cyanide species and other species of the individual metal ions can be used to indicate possible reactions between metal cyanide species and other species of different metals such as cations and oxides. This subject is treated subsequently in this chapter.

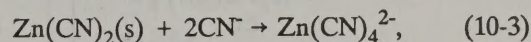
### *Hexacyanometallates*

The hexacyanometallates of Co(III), Fe(II), Fe(III), Mn(III), and Cr(III) all give precipitates with heavy metal cations (1-2). Of these, the heavy-metal hexacyanoferrates are the best known. These compounds nearly always form as colloids or gelatinous precipitates that are not stoichiometric. They contain variable quantities of the alkali ion from the hexacyanometallate salt and variable quantities of water of hydration. Alkali metal ions can be excluded from the precipitates by using an excess of heavy-metal cation. Because of these compositional variations, there are few quantitative studies of their solubility equilibria, and the available data are of uncertain reliability. Solubility-product data for hexacyanoferrate precipitates (3-12) are compiled in table 10-1.

## REACTIONS BETWEEN METAL CYANIDE SPECIES AND METAL CATIONS OR OXIDE SPECIES

### *General*

In cyanide solutions in which there is insufficient  $\text{CN}^-$  to form soluble species of all cyanide-reactive metals, it is important to know the speciation of different metals and the reactions that may occur between these species. In such cyanide-deficient systems, metals may precipitate as cyanides, oxide species, or compounds with accessory anions such as  $\text{CO}_3^{2-}$ . The equilibrium data for metal cyanide and oxide species (appendix D) can be used to predict the reactions of individual metal species and the reactions between cyanide species and cations and oxide species of different metals. In considering these reactions, a convenient quantity to use is the ratio of log K for the reaction to the number of moles,  $n$ , of  $\text{CN}^-$  transferred. For example, for the reaction



log K from table D-2 = +4.0, and  $n = 2$ , so  $(\log K)/n = +2.0$ . Values of  $(\log K)/n$  for several reactions are compiled in table 10-2. In table 10-2, the reactions are arranged in order of decreasing  $(\log K)/n$ , constituting a replacement series, which is analogous to the "electromotive force" series used in connection with metal cementation. Metal cations will displace  $\text{CN}^-$  from metal cyanide species with lower values of  $(\log K)/n$ .

In table 10-2, the reactions for the metal species could be rewritten with HCN instead of  $\text{CN}^-$  on the left sides of the equations. The  $(\log K)/n$  values for the rewritten reactions would all be more negative by 9.2 log units than the tabulated values.

Note in table 10-2 that the values of  $(\log K)/n$  for the hexacyanoferrates are intermediate. The hexacyanoferrates are often thought of as being stable complexes. Thermodynamically, the hexacyanoferrates are of intermediate stability; kinetic factors are responsible for their inertness. The iron cyanide complexes are discussed further below as well as in chapters 8 and 9.

Table 10-2 portrays an oversimplified picture of reactions between different metals in cyanide systems, because cyanide solutions are alkaline, and metal oxide species are present. Table 10-3 lists  $(\log K)/n$  values for reactions of metal oxide compounds with  $\text{CN}^-$ , in the same format as table 10-2.



Table 10-1.-Solubility products of some heavy-metal hexacyanoferrates at 25° C

Cation	-Log $K_{so}$		$^1\Delta_f G^\circ$
	Reported	Selected	
$M_4Fe(CN)_6$ :			
Cu	N	<sup>2</sup> 42	696.9
Ag	38-44	38	832.5
Hg <sup>3</sup>	N	<sup>4</sup> 26	899.8
$M_2Fe(CN)_6$ :			
Pb	16-18	17	596.0
Zn	14-17	16	355.7
Cd	15-17	16	494.5
Hg	N	<sup>5</sup> 20	956.0
Cu	14-17	16	780.1
Ni	13-15	16	560.9
Co	15-16	16	538.1
Mn	N	<sup>6</sup> 15	193.4
$M_3Fe(CN)_6$ :			
Cu	N	<sup>7</sup> 35	722.9
Ag	28	28	847.5
Hg <sup>3</sup>	<sup>8</sup> 18	18	903.7
$M_3[Fe(CN)_6]_2$ :			
Pb	N	<sup>9</sup> 18	1,377.3
Zn	N	<sup>9</sup> 18	1,008.3
Cd	18	18	1,216.5
Hg	N	<sup>5</sup> 22	1,920.2
Cu	24	<sup>9</sup> 20	1,633.4
Ni	N	<sup>9</sup> 20	1,304.6
Co	N	<sup>9</sup> 20	1,270.4
Mn	14-18	18	756.3

N No data.

<sup>1</sup>Calculated from selected value of log  $K_{so}$  and  $\Delta_f G^\circ$  data in tables in appendix D.

<sup>2</sup>Estimated from data for Ag(I) compound and for Cu(I) and Ag(I) complexes with  $CH_3CN$  in references 5 and 6.

<sup>3</sup>(1/2)Hg<sub>2</sub><sup>2+</sup>.

<sup>4</sup>Taken as 10 units higher than mean value for Zn, Cd, etc. analogs, by proportion to data for corresponding  $[Fe(CN)_6]^{3-}$  compounds.

<sup>5</sup>Estimated as less soluble than Zn, Cd, etc. analogs.

<sup>6</sup>Estimated as 1 unit lower than mean value of Zn, Cd, etc. analogs, by proportion to data for corresponding  $[Fe(CN)_6]^{3-}$  compounds.

<sup>7</sup>Estimated by same consideration as for  $[Fe(CN)_6]^{4-}$  compound, with increase for interaction due to mixed Cu oxidation states.

<sup>8</sup>Estimated as approximately equal to value for  $[Co(CN)_6]^{3-}$  analog in reference 5.

<sup>9</sup>Estimated as comparable to values for Cd and Mn compounds, as is the case for corresponding  $[Fe(CN)_6]^{4-}$  compounds.

Note: Reported data (3-12) vary as indicated by ranges in values, owing to variations in composition.

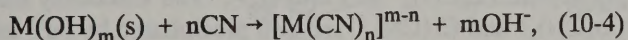


Table 10-2.-Relative stabilities of some metal cyanide complexes

Reaction (X = CN)			(log K)/n <sup>1</sup>
Cu <sup>+</sup>	+ X <sup>-</sup>	→ CuX(s)	19.5
Hg <sup>2+</sup>	+ 2X <sup>-</sup>	→ HgX <sub>2</sub> (s)	16.4
Ag <sup>+</sup>	+ X <sup>-</sup>	→ AgX(s)	15.7
Tl <sup>3+</sup>	+ 2X <sup>-</sup>	→ TlX <sub>2</sub> <sup>+</sup>	13.0
Co <sup>3+</sup>	+ 6X <sup>-</sup>	→ CoX <sub>6</sub> <sup>3-</sup>	(12.17)
Ni <sup>2+</sup>	+ 2X <sup>-</sup>	→ NiX <sub>2</sub> (s)	9.75
H <sup>1+</sup>	+ X <sup>-</sup>	→ HX	9.2
Fe <sup>2+</sup>	+ 2X <sup>-</sup>	→ (1/3)Fe <sub>2</sub> Fe(CN) <sub>6</sub> (s)	(8.55)
Zn <sup>2+</sup>	+ 2X <sup>-</sup>	→ ZnX <sub>2</sub> (s)	7.8
Fe <sup>3+</sup>	+ 6X <sup>-</sup>	→ FeX <sub>6</sub> <sup>3-</sup>	7.05
TlX <sub>2</sub> <sup>+</sup>	+ 2X <sup>-</sup>	→ TlX <sub>4</sub> <sup>-</sup>	7.0
Fe <sup>2+</sup>	+ 6X <sup>-</sup>	→ FeX <sub>6</sub> <sup>4-</sup>	5.9
Mn <sup>3+</sup>	+ 6X <sup>-</sup>	→ MnX <sub>6</sub> <sup>3-</sup>	(5.83)
Cd <sup>2+</sup>	+ 2X <sup>-</sup>	→ CdX <sub>2</sub> (s)	5.55
Cr <sup>3+</sup>	+ 6X <sup>-</sup>	→ CrX <sub>6</sub> <sup>3-</sup>	(5.5)
NiX <sub>2</sub> (s)	+ 2X <sup>-</sup>	→ NiX <sub>4</sub> <sup>2-</sup>	5.35
(1/3)Fe <sub>2</sub> Fe(CN) <sub>6</sub>	+ 4X <sup>-</sup>	→ FeX <sub>6</sub> <sup>4-</sup>	(4.58)
AgX(s)	+ X <sup>-</sup>	→ AgX <sub>2</sub> <sup>-</sup>	4.8
CuX(s)	+ 2X <sup>-</sup>	→ CuX <sub>3</sub> <sup>2-</sup>	3.75
CdX <sub>2</sub>	+ 2X <sup>-</sup>	→ CdX <sub>4</sub> <sup>2-</sup>	3.4
HgX <sub>2</sub>	+ 2X <sup>-</sup>	→ HgX <sub>4</sub> <sup>2-</sup>	3.1
ZnX <sub>2</sub> (s)	+ 2X <sup>-</sup>	→ ZnX <sub>4</sub> <sup>2-</sup>	2.0
Mn <sup>2+</sup>	+ 6X <sup>-</sup>	→ MnX <sub>6</sub> <sup>4-</sup>	(1.67)

<sup>1</sup>n is the number of free CN<sup>-</sup> (= X) on left side of reaction equation. Values in parentheses are estimated. Data are from tables in appendix D.

To compare different metal-cyanide reactions as a function of pH, it is necessary to write equations to express the pH dependence. For a reaction



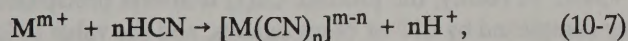
define

$$(\log K^*)/n = (\log K)/n = (m/n) \log [OH^-] \quad (10-5)$$

or

$$(\log K^*)/n = (\log K)/n + (m/n) (14 - pH). \quad (10-6)$$

Similarly, for a reaction in acid solution



write

$$(\log K^*)/n = (\log K)/n + (1/n) (pH). \quad (10-8)$$

Plots of (log K<sup>\*</sup>)/n versus pH in accordance with equations 10-6 and 10-8 for different metal-cyanide reactions are shown in figure 10-1. At pH below 9.2, HCN is the predominant free cyanide species, and all reactions are written with HCN instead of CN<sup>-</sup>, and their (log K<sup>\*</sup>)/n values are computed and plotted accordingly. Figure 10-1 may be used as a replacement series in the same way as mentioned for table 10-2. At a given pH value, metal cations or oxide species displace CN<sup>-</sup> from metal cyanide species with lower values of (log K<sup>\*</sup>)/n.

Examples of the use of tables 10-2 and 10-3 and figure 10-1 are given in chapter 11, in which examples of practical equilibrium problems are provided.

#### Reactions Involving Iron

The toxicity of cyanide species may be rapidly and inexpensively mitigated by addition of Fe(II) salts, which react with free CN<sup>-</sup> and the CN<sup>-</sup> in WAD cyanide species to form [Fe(CN)<sub>6</sub>]<sup>4-</sup>. The [Fe(CN)<sub>6</sub>]<sup>4-</sup> may undergo oxidation to [Fe(CN)<sub>6</sub>]<sup>3-</sup>. Photochemical decomposition of



Table 10-3.--Some reactions of metal oxide compounds with cyanide

Reaction (X = CN)					(log K)/n <sup>1</sup>
Ag <sub>2</sub> O(s)	+	H <sub>2</sub> O + 2X <sup>-</sup>	→	2AgX(s) + 2OH <sup>-</sup>	+8.0
Ag <sub>2</sub> O(s)	+	H <sub>2</sub> O + 4X <sup>-</sup>	→	2AgX <sub>2</sub> <sup>-</sup> + 2OH <sup>-</sup>	+6.4
Hg(OH) <sub>2</sub>		+ 2X <sup>-</sup>	→	HgX <sub>2</sub> + 2OH <sup>-</sup>	+5.5
Cu <sub>2</sub> O(s)	+	H <sub>2</sub> O + 2X <sup>-</sup>	→	2CuX(s) + 2OH <sup>-</sup>	+4.8
Hg(OH) <sub>2</sub>		+ 4X <sup>-</sup>	→	HgX <sub>4</sub> <sup>2-</sup> + 2OH <sup>-</sup>	+4.3
Cu <sub>2</sub> O(s)	+	H <sub>2</sub> O + 6X <sup>-</sup>	→	2CuX <sub>3</sub> <sup>2-</sup> + 2OH <sup>-</sup>	+4.1
HgO(s)	+	H <sub>2</sub> O + 2X <sup>-</sup>	→	HgX <sub>2</sub> + 2OH <sup>-</sup>	+3.7
HgO(s)	+	H <sub>2</sub> O + 4X <sup>-</sup>	→	HgX <sub>4</sub> <sup>2-</sup> + 2OH <sup>-</sup>	+3.4
Fe(OH) <sub>2</sub> (s)		+ 6X <sup>-</sup>	→	FeX <sub>6</sub> <sup>2-</sup> + 2OH <sup>-</sup>	+3.37
Ni(OH) <sub>2</sub> (s)		+ 4X <sup>-</sup>	→	NiX <sub>4</sub> <sup>2-</sup> + 2OH <sup>-</sup>	+3.25
Ni(OH) <sub>2</sub> (s)		+ 2X <sup>-</sup>	→	NiX <sub>2</sub> (s) + 2OH <sup>-</sup>	+1.15
Fe(OH) <sub>2</sub> (s)		+ 2X <sup>-</sup>	→	(1/3)Fe <sub>2</sub> FeX <sub>6</sub> (s) + 2OH <sup>-</sup>	(+0.95)
Cd(OH) <sub>2</sub> (s)		+ 4X <sup>-</sup>	→	CdX <sub>4</sub> <sup>2-</sup> + 2OH <sup>-</sup>	+0.88
ZnO(s)	+	H <sub>2</sub> O + 4X <sup>-</sup>	→	ZnX <sub>4</sub> <sup>2-</sup> + 2OH <sup>-</sup>	+0.72
Cr(OH) <sub>3</sub> (s)		+ 6X <sup>-</sup>	→	CrX <sub>6</sub> <sup>3-</sup> + 3OH <sup>-</sup>	(+0.17)
FeO(OH)(s)	+	H <sub>2</sub> O + 6X <sup>-</sup>	→	FeX <sub>6</sub> <sup>3-</sup> + 3OH <sup>-</sup>	+0.1
Mn(OH) <sub>2</sub> (s)		+ 6X <sup>-</sup>	→	MnX <sub>6</sub> <sup>4-</sup> + 2OH <sup>-</sup>	(-0.47)
ZnO(s)	+	H <sub>2</sub> O + 2X <sup>-</sup>	→	ZnX <sub>2</sub> (s) + 2OH <sup>-</sup>	-0.55
Tl <sub>2</sub> O <sub>3</sub> (s)	+	3H <sub>2</sub> O + 8X <sup>-</sup>	→	2TlX <sub>4</sub> <sup>-</sup> + 6OH <sup>-</sup>	-1.18
MnO(OH)(s)	+	H <sub>2</sub> O + 6X <sup>-</sup>	→	MnX <sub>6</sub> <sup>3-</sup> + 3OH <sup>-</sup>	(-1.2)
Cd(OH) <sub>2</sub> (s)		+ 2X <sup>-</sup>	→	CdX <sub>2</sub> + 2OH <sup>-</sup>	-1.65

<sup>1</sup>n is the number of free CN<sup>-</sup> (= X) on left side of reaction equation. Values in parentheses are estimated. Data are from tables in appendix D.

[Fe(CN)<sub>6</sub>]<sup>4-</sup> and [Fe(CN)<sub>6</sub>]<sup>3-</sup> liberates CN<sup>-</sup>, so the practice of adding Fe(II) salts to lower cyanide toxicity may be counterproductive. However, if [Fe(CN)<sub>6</sub>]<sup>4-</sup> and [Fe(CN)<sub>6</sub>]<sup>3-</sup> are precipitated by metal cations such as excess Fe<sup>2+</sup>, the precipitates may resist photochemical decomposition. Complete precipitation of [Fe(CN)<sub>6</sub>]<sup>4-</sup> and [Fe(CN)<sub>6</sub>]<sup>3-</sup> generally requires that the pH be near 7. The reactions of some metal cations and oxide species in the presence of [Fe(CN)<sub>6</sub>]<sup>4-</sup> are illustrated in equilibrium predominance area diagrams (EPAD) in figures E-17, E-39, E-148, E-97, E-165, E-167, and E-168.

Tables 10-2 and 10-3 and figure 10-1 can be used for predicting reactions in which [Fe(CN)<sub>6</sub>]<sup>4-</sup> is formed, but not reactions in which [Fe(CN)<sub>6</sub>]<sup>4-</sup> would be decomposed, owing to its kinetic inertness. They are useful for predicting the reactions of added Fe<sup>2+</sup>, e.g., FeSO<sub>4</sub>, with different metal cyanide species. Figure 10-1 shows that Fe(OH)<sub>2</sub>(s) reacts with different metal cyanide species at pH near 11 to form [Fe(CN)<sub>6</sub>]<sup>4-</sup> and the reaction product of the other metal as follows:

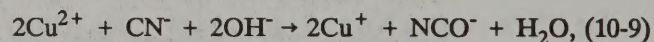
Zn: Converted to oxide species  
 Cd: Converted to oxide species  
 Hg: Converted to Hg(CN)<sub>2</sub> or Hg(OH)(CN)  
 Cu: Converted to CuCN(s)

Ag: Converted to AgCN(s)  
 Ni: No reaction  
 Mn: Converted to oxide species

At pH near 7, the metal oxide species may react to precipitate Fe(CN)<sub>6</sub><sup>4-</sup> or Fe(CN)<sub>6</sub><sup>3-</sup>. The kinetically inert Co(CN)<sub>6</sub><sup>3-</sup> and Cr(CN)<sub>6</sub><sup>3-</sup> are also precipitated by Fe<sup>2+</sup> and other heavy-metal cations at pH near 7.

#### Reactions Involving Copper(II)

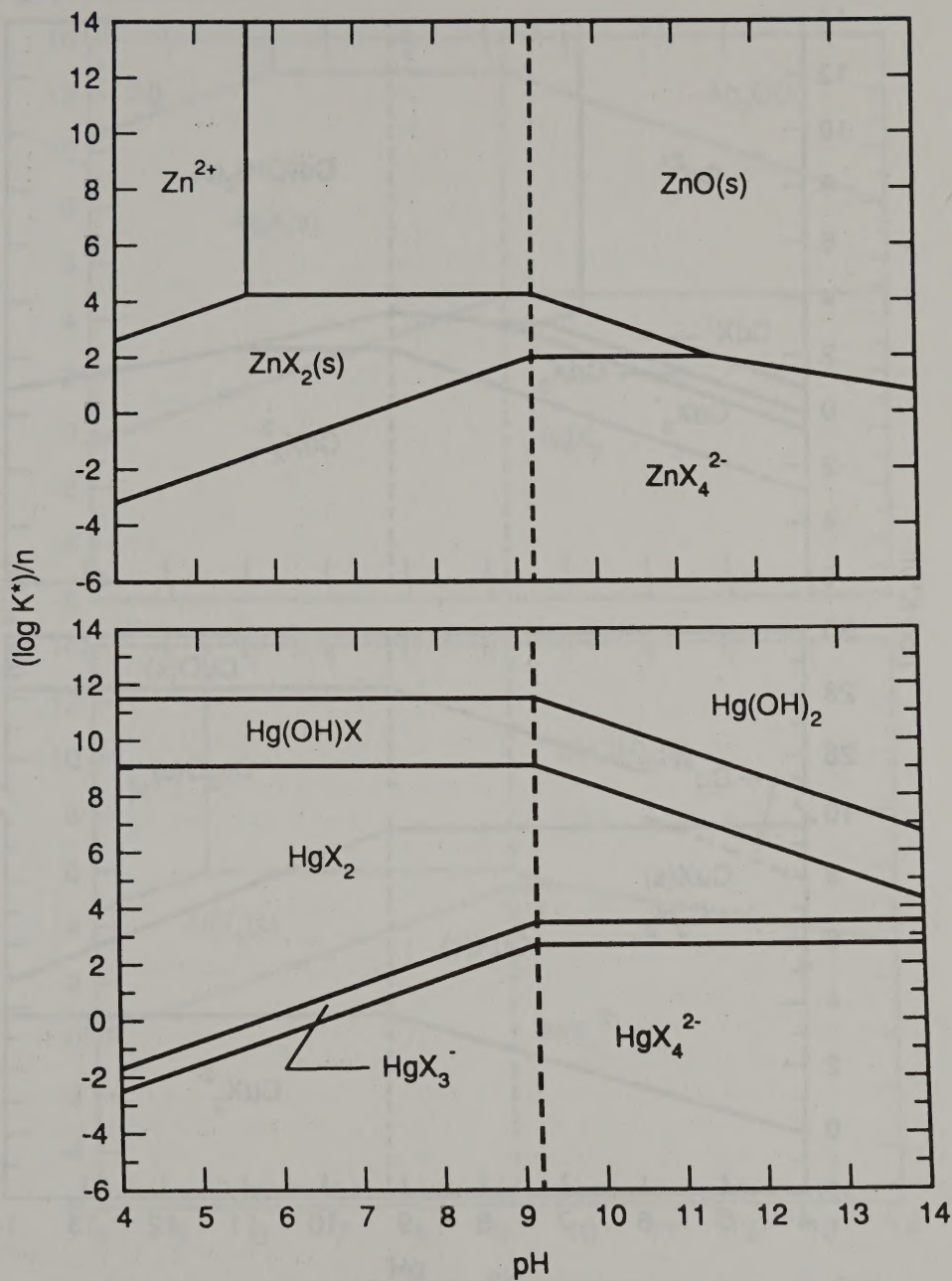
As noted in chapter 8, Cu(II) oxidizes CN<sup>-</sup> and is reduced to Cu(I). The reaction



with uncomplexed Cu(I) as product, has a log K value of +39.4. In reality, the product Cu(I) is always precipitated or complexed by CN<sup>-</sup> or other ligands, and the value of log K is larger. Data for the reactions are compiled in table 10-4. In table 10-4, values of (log K)/n, where n is the number of moles of CN<sup>-</sup> reacting, are also listed, as in table 10-3. The values of log K are so large that Cu(II) in any form, such as CuO, ammonia complexes, or EDTA complex, oxidizes CN<sup>-</sup>. Values of (log K\*)/n, defined as



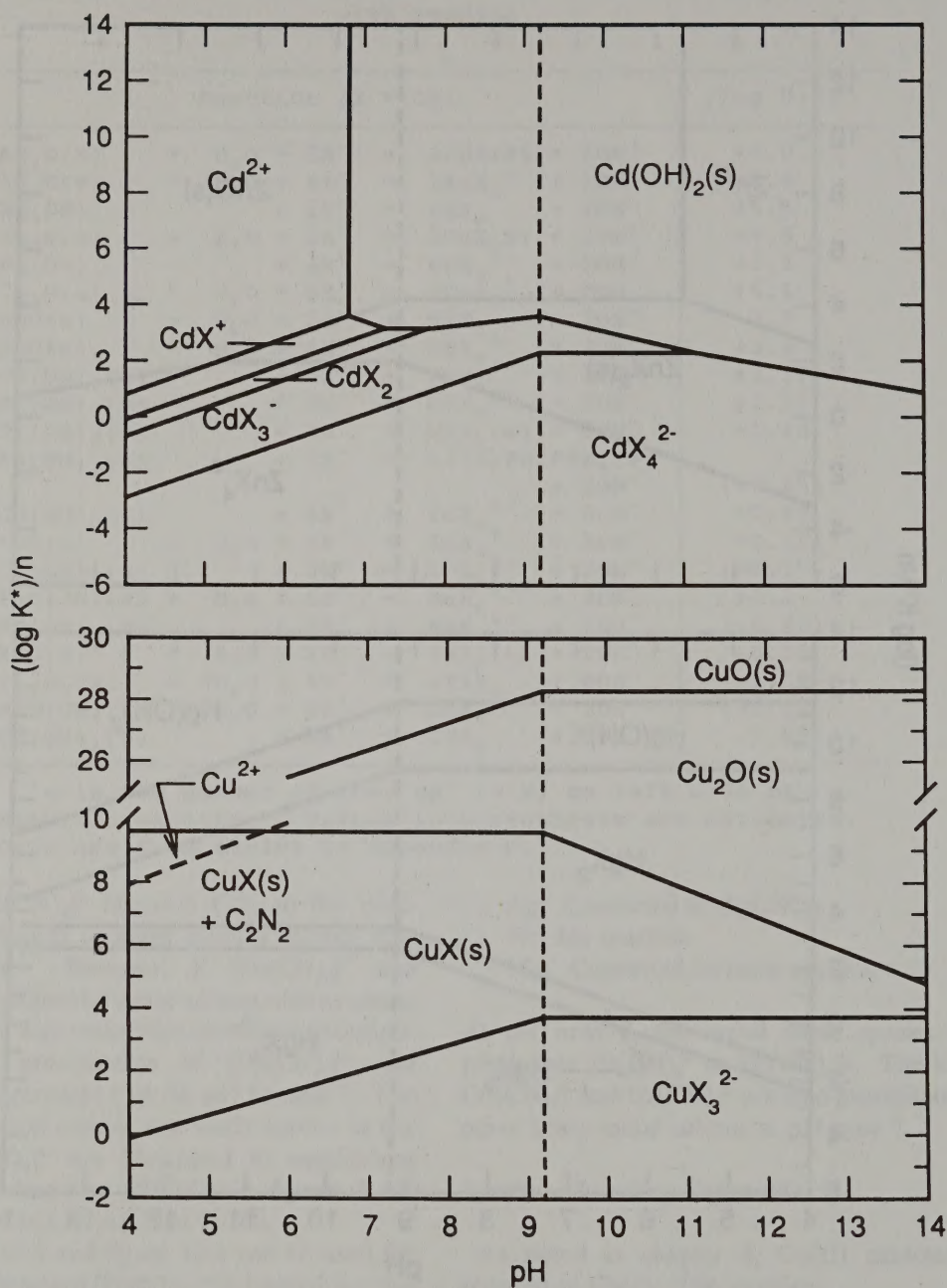
Figure 10-1



Plots of  $(\log K^*)/n$  for metal cyanide species. Superposition of plots for different metal ions provides a replacement series for metal cyanide species. In each diagram, X in formulas denotes CN<sup>-</sup>; the plots all show breaks at  $pH = 9.2 = pK_a$  of HCN.



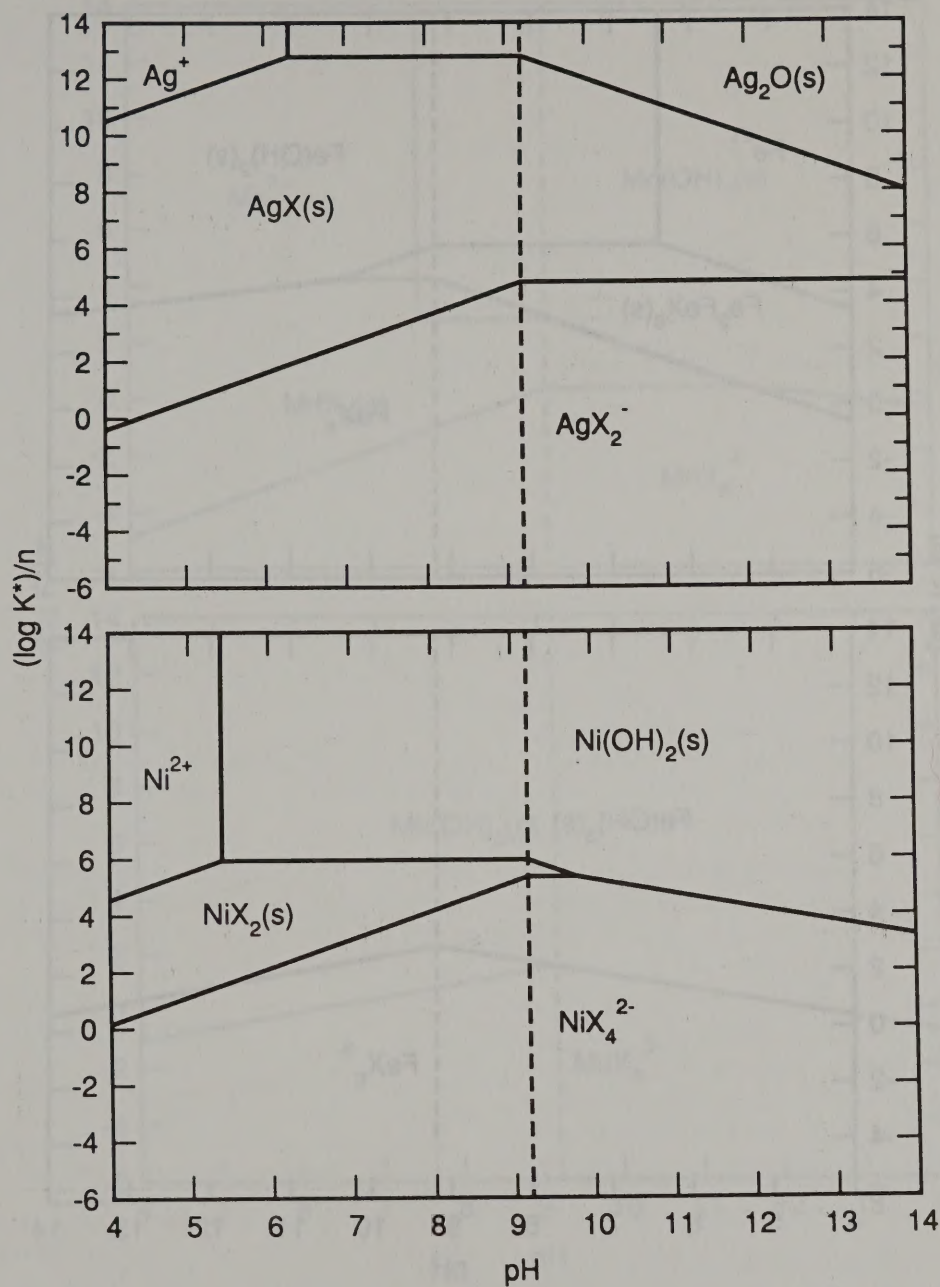
Figure 10-1-Continued



Plots of  $(\log K^*)/n$  for metal cyanide species. Superposition of plots for different metal ions provides a replacement series for metal cyanide species. In each diagram, X in formulas denotes CN; the plots all show breaks at  $\text{pH} = 9.2 = \text{p}K_a$  of HCN.



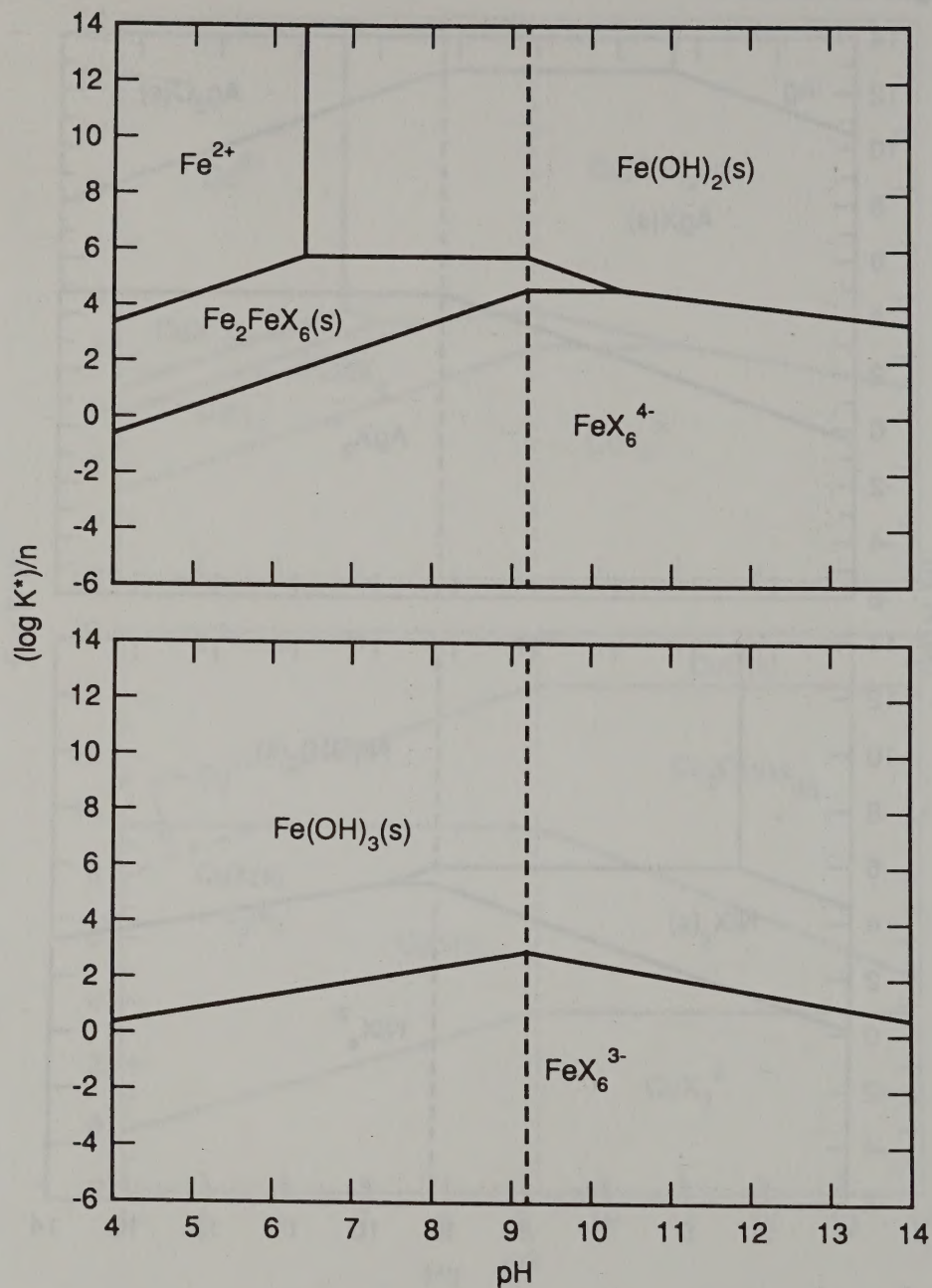
Figure 10-1-Continued



Plots of  $(\log K^*)/n$  for metal cyanide species. Superposition of plots for different metal ions provides a replacement series for metal cyanide species. In each diagram, X in formulas denotes CN<sup>-</sup>; the plots all show breaks at  $\text{pH} = 9.2 = \text{p}K_a$  of HCN.



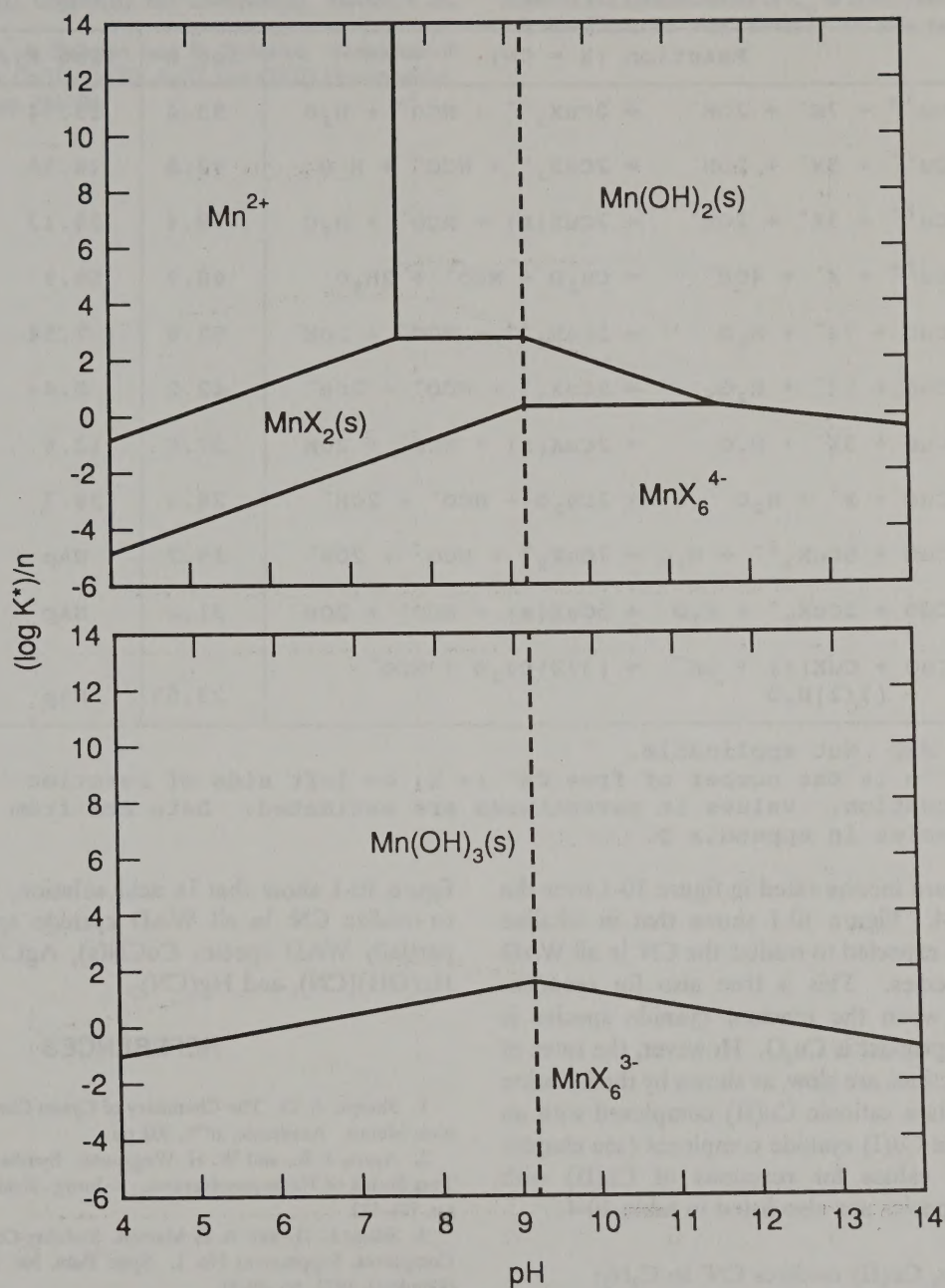
Figure 10-1-Continued



Plots of  $(\log K^*)/n$  for metal cyanide species. Superposition of plots for different metal ions provides a replacement series for metalocyanide species. In each diagram, X in formulas denotes CN; the plots all show breaks at  $\text{pH} = 9.2 = \text{p}K_a$  of HCN.



Figure 10-1-Continued



Plots of  $(\log K^*)/n$  for metal cyanide species. Superposition of plots for different metal ions provides a replacement series for metal cyanide species. In each diagram, X in formulas denotes CN<sup>-</sup>; the plots all show breaks at  $\text{pH} = 9.2 = \text{p}K_a$  of HCN.



Table 10-4.--Reactions of copper(II) with cyanide species

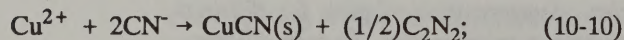
Reaction (X = CN)	log K	(log K)/n <sup>1</sup>
$2\text{Cu}^{2+} + 7\text{X}^- + 2\text{OH}^- \rightarrow 2\text{CuX}_3^{2-} + \text{NCO}^- + \text{H}_2\text{O}$	93.4	13.34
$2\text{Cu}^{2+} + 5\text{X}^- + 2\text{OH}^- \rightarrow 2\text{CuX}_2^- + \text{NCO}^- + \text{H}_2\text{O}$	82.8	16.56
$2\text{Cu}^{2+} + 3\text{X}^- + 2\text{OH}^- \rightarrow 2\text{CuX(s)} + \text{NCO}^- + \text{H}_2\text{O}$	78.4	26.13
$2\text{Cu}^{2+} + \text{X}^- + 4\text{OH}^- \rightarrow \text{Cu}_2\text{O} + \text{NCO}^- + 2\text{H}_2\text{O}$	68.9	68.9
$2\text{CuO} + 7\text{X}^- + \text{H}_2\text{O} \rightarrow 2\text{CuX}_3^{2-} + \text{NCO}^- + 2\text{OH}^-$	52.8	7.54
$2\text{CuO} + 5\text{X}^- + \text{H}_2\text{O} \rightarrow 2\text{CuX}_2^- + \text{NCO}^- + 2\text{OH}^-$	42.2	8.44
$2\text{CuO} + 3\text{X}^- + \text{H}_2\text{O} \rightarrow 2\text{CuX(s)} + \text{NCO}^- + 2\text{OH}^-$	37.8	12.6
$2\text{CuO} + \text{X}^- + \text{H}_2\text{O} \rightarrow 2\text{Cu}_2\text{O} + \text{NCO}^- + 2\text{OH}^-$	28.3	28.3
$2\text{CuO} + 5\text{CuX}_3^{2-} + \text{H}_2\text{O} \rightarrow 7\text{CuX}_2^- + \text{NCO}^- + 2\text{OH}^-$	15.7	NAP
$2\text{CuO} + 3\text{CuX}_2^- + \text{H}_2\text{O} \rightarrow 5\text{CuX(s)} + \text{NCO}^- + 2\text{OH}^-$	31.2	NAP
$2\text{CuO} + \text{CuX(s)} + \text{OH}^- \rightarrow (3/2)\text{Cu}_2\text{O} + \text{NCO}^- + (1/2)\text{H}_2\text{O}$	23.55	NAP

NAP Not applicable.

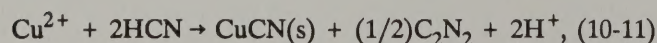
<sup>1</sup>n is the number of free CN<sup>-</sup> (= X) on left side of reaction equation. Values in parentheses are estimated. Data are from tables in appendix D.

in equation 10-6, are incorporated in figure 10-1 over the pH range 6 to 14. Figure 10-1 shows that in alkaline solution, Cu(II) is expected to oxidize the CN<sup>-</sup> in all WAD metal cyanide species. This is true also for cyanocuprate(I) species; when the reactant cyanide species is CuCN, the Cu(I) product is Cu<sub>2</sub>O. However, the rates of some of these reactions are slow, as shown by the isolation of solids that contain cationic Cu(II) complexed with an amine, and anionic Cu(I) cyanide complexes (see chapter 8). The log K values for reactions of Cu(II) with cyanocuprate(I) species are also listed in table 10-4.

In acid solution, Cu(II) oxidizes CN<sup>-</sup> to C<sub>2</sub>N<sub>2</sub>:



log K = +26.2, n = 2, and (log K)/n = +13.1, which may be compared with the other data in table 10-2. For the reaction



log K = +7.8 and (log K)/n = +3.9. Values of (log K\*)/n, defined as in equation 10-8, are incorporated in figure 10-1 over the pH range 0 to 6. Table 10-2 and

figure 10-1 show that in acid solution, Cu<sup>2+</sup> is expected to oxidize CN<sup>-</sup> in all WAD cyanide species except the partially WAD species CuCN(s), AgCN(s), [Hg(CN)]<sup>+</sup>, Hg(OH)(CN), and Hg(CN)<sub>2</sub>.

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## CHAPTER 11.—SOLUTION OF CHEMICAL EQUILIBRIUM PROBLEMS

### INTRODUCTION

In mineral processing and mine decommissioning activities, it is important to know what chemical reactions can occur in connection with the disposal or fate of cyanides. The first question to be answered is, "What chemical reactions may be expected to occur, and to what extent?" In other words, what chemical reactions are thermodynamically possible, and what are the important chemical equilibria? The second question is, "What are the reaction rates?"; this subject is addressed in chapter 12.

The answer to the question of equilibria requires thermodynamic data for the pertinent species and reactions. This publication contains many data on pertinent species and reactions in appendixes B, C, D, and E. The objective of this chapter is to show how the data in this publication may be used to obtain semiquantitative or qualitative yes/no solutions to practical chemical equilibrium problems. This chapter will show (1) the use of equilibrium predominance area diagrams (EPAD) and (2) the calculation of reaction equilibrium constants to obtain semiquantitative solutions to chemical equilibrium problems.

This chapter does not provide procedures for obtaining detailed quantitative information on solubilities and species concentrations. The required detailed calculations are best done by computer. Readers interested in such details should consult pertinent literature and published computer programs (1-7).<sup>1</sup>

### EXAMPLES OF THE USE OF EQUILIBRIUM PREDOMINANCE AREA DIAGRAMS

A collection of EPAD is useful for qualitative or semiquantitative examination of a chemical system. It shows what chemical species prevail under specified conditions and ranges of composition, and what reactions may be expected if the composition of the system is changed, e.g., by altering the pH or destroying excess  $\text{CN}^-$  with an oxidant. This section contains several examples that illustrate the use of EPAD in solving practical chemical equilibrium problems.

EPAD by definition show the predominant species in a system as a function of composition variables, often at constant temperature and pressure. Two of the composition variables are assigned to the coordinate axes of the diagram, and the others are held constant. The thermodynamic basis of EPAD, definitions of the composition

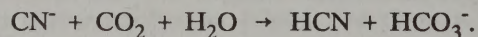
variables, and the varieties of EPAD are outlined in chapter 4. A collection of EPAD is presented in appendix E. The EPAD in appendix E are drawn for selected values of the composition variables that are held constant. For intermediate values of those composition variables, the desired results may be obtained by interpolation from the two diagrams that bracket the value of that composition variable.

#### Example 1: Cyanide Safety

EPAD can be used to verify whether cyanide mixture compositions may pose a safety hazard. At what free cyanide concentrations and pH values do cyanide solutions have safe HCN partial pressures? To answer this, the pL-pH diagram for free cyanide, figure E-1, is used. Figure E-1 shows the isobars for specified HCN partial pressures,  $p(\text{HCN})$ , overlaid on the solution-species predominance areas for HCN and  $\text{CN}^-$ . Note that the maximum allowable concentration = 10 ppm ( $1 \times 10^{-5}$  bar line) for  $p(\text{HCN})$ . All solution compositions below and to the right of that line have safe  $p(\text{HCN})$  values. A leach solution with 0.5 kg NaCN per metric ton ( $0.5 \text{ g} \cdot \text{L}^{-1}$ ) solution is 0.010M in NaCN, so  $p\text{L} = p\text{CN} = 2.0$ . Figure E-1 shows that at  $p\text{CN} = 2.0$ , the pH must be at least 11.35 to maintain  $p(\text{HCN})$  below 10 ppm. If the pH were 11.0,  $p(\text{HCN})$  would be about 20 ppm.

#### Example 2: Cyanide and Carbonates

It is necessary to maintain cyanide solutions at pH 10 to 11 to avoid loss of HCN. Atmospheric  $\text{CO}_2$  is sufficiently acidic to liberate HCN from solutions containing free  $\text{CN}^-$  or weak-acid dissociable (WAD) cyanide complexes:



The compatibility of cyanide and carbonate solutions is of interest in view of this fact. What happens when cyanide and carbonate solutions of different speciation are mixed? To answer this question, the pL-pH diagram for carbonate, figure E-2, is required in addition to that for cyanide, figure E-1. Superposition of the two diagrams shows what species coexist and what species would react. Mixing carbonated water with NaCN solution would result in liberation of HCN. The carbonated water, with  $\text{CO}_2$  predominant, has pH below 6.3, while the NaCN solution, with  $\text{CN}^-$  predominant, has pH above 9.2. The predominance areas for  $\text{CO}_2$  and  $\text{CN}^-$  do not overlap, so those species cannot

<sup>1</sup>Italic numbers in parentheses refer to items in the list of references at the end of this chapter.



coexist as predominant species in the same solution. Further, HCN and  $\text{HCO}_3^-$  can coexist as predominant species at pH 6.3 to 9.2. The EPAD thus show that  $\text{CO}_2$  and  $\text{CN}^-$  react to give HCN and  $\text{HCO}_3^-$ .

### Example 3: Cyanide and Carbon Dioxide

Cyanide solutions can react with  $\text{CO}_2$  from the air and liberate HCN, as discussed in the preceding example. The extent to which this reaction occurs bears on safety considerations and cyanide losses. The partial pressure of  $\text{CO}_2$  is roughly a hundred times higher in exhaled air than in fresh air, which is a major reason for supplying efficient ventilation to personnel working with cyanide solutions. At what compositions do cyanide solutions absorb  $\text{CO}_2$  from the air? Figure E-2 shows isobars for  $\text{CO}_2$  partial pressures for fresh air and for exhaled air,  $\log p(\text{CO}_2) = -3.4$  and  $-1.4$ , respectively. Carbonate solutions with compositions below and to the right of the  $\log p(\text{CO}_2) = -3.4$  isobar will absorb  $\text{CO}_2$  from fresh air; solutions with compositions on the other side of that isobar will not absorb  $\text{CO}_2$  from fresh air. Superposition of figures E-1 and E-2 shows that NaCN leach solutions with pH around 11 will absorb  $\text{CO}_2$  from fresh air, because all pH 11 solution compositions lie below or to the right of the fresh-air  $\text{CO}_2$  isobar. This fact confirms the importance of monitoring and maintaining sufficient alkalinity in cyanide leach solutions.

### Example 4: Zinc Species in Cyanide Solutions

When metallic zinc is used to cement precious metals from cyanide solutions, it is converted to undissolved solids or dissolved species. The zinc concentration in the barren solutions and the zinc-containing solids may affect procedures for recycle or disposal of these solutions. The identity of zinc-containing solids is important because  $\text{Zn}(\text{CN})_2$  has a low solubility. The extent to which zinc in cyanide solutions may interfere with leaching also deserves attention. This and several succeeding examples bear on this problem and show the versatility of EPAD for solving these problems. The approaches used to solve problems here can be adapted to deal with other metals in cyanide solutions.

What is the speciation of zinc in cyanide solutions? The extent to which zinc is complexed in cyanide solutions may affect the effectiveness of the solutions for leaching more ore. An effective picture is presented by a pL-pH EPAD,  $L = \text{CN}$ , for dissolved zinc species, figure E-19. The predominance areas of dissolved species are independent of zinc concentration or the presence of any zinc oxide or cyanide solid phases; they depend only on pH and

pCN. In a zinc-containing leach solution with pCN = 2.0, i.e., free  $\text{CN}^- = 1 \times 10^{-2}M$  (260 ppm), and pH 11.0, the predominant zinc species is  $[\text{Zn}(\text{CN})_4]^{2-}$ . It is important to remember that pL refers to free, not total ligand concentration. In this example, free  $\text{CN}^-$  is  $1 \times 10^{-2}M$ . Total  $\text{CN}^-$  is free  $\text{CN}^-$  plus the  $\text{CN}^-$  complexed with zinc. If total zinc is  $1 \times 10^{-3}M$ , total  $\text{CN}^- = 0.010 + 4(0.001) = 0.014M$ . A calculation such as this one is approximate to the extent that the predominant species constitutes less than 100 pct of the total, and should be regarded as semiquantitative.

Suppose a solution contains  $1 \times 10^{-3}M$  total  $\text{CN}^-$  (26 ppm),  $2 \times 10^{-4}M$  Zn (13 ppm), and has pH 10.0. This composition may be similar to that of a diluted barren solution. What is the predominant zinc species? To the extent that  $\text{CN}^-$  is complexed with zinc, free  $\text{CN}^-$  is less than total  $\text{CN}^-$ . If the zinc were 100 pct  $[\text{Zn}(\text{CN})_4]^{2-}$ , free  $\text{CN}^-$  would be  $0.001 - 4(0.0001) = 0.0006M$ . This means that free  $\text{CN}^-$  is between  $6 \times 10^{-4}$  and  $1 \times 10^{-3}M$ , i.e., pCN is between 3.2 and 3.0. For pCN = 3.0 to 3.2 and pH = 10.0, figure E-19 shows that the predominant zinc species is  $[\text{Zn}(\text{CN})_4]^{2-}$ . This region on the diagram is close to the boundary with the predominance area for  $[\text{Zn}(\text{CN})_3]^-$ , so the latter species will contribute a significant fraction of the total zinc species.

It should be noted that on a boundary line separating the areas for two predominant solution species, those species coexist at equal concentrations. At a point where the areas of three predominant solution species meet, the three species coexist at equal concentrations. Near such a point, the predominant species will constitute less than 50 pct of the total species. Predominance of species has the same sense as plurality, not majority, as in an election with more than two candidates. The further a point in a solution-species predominance area is from any boundary of that area, the more nearly that predominant species constitutes 100 pct of the total species in the solution. For example, in figure E-19, the point at pH 11.0 and pCN 1.0 in the  $[\text{Zn}(\text{CN})_4]^{2-}$  predominance area is at least 2 pH and 2 pCN units away from any boundary of the area, so nearly all zinc exists as  $[\text{Zn}(\text{CN})_4]^{2-}$ .

In a solution with free  $\text{CN}^- = 0.1 \text{ ppm} = 4 \times 10^{-6}M$ , i.e., pCN = 5.4, figure E-19 shows that the predominant dissolved zinc species contain no  $\text{CN}^-$ , regardless of pH.

### Example 5: Precipitation of Zinc Cyanide in Cyanide Systems

Under some conditions, it may be advisable to remove zinc from cyanide solutions before reuse. To minimize cyanide losses in separated solids, it is of interest to avoid precipitation of solids that contain  $\text{CN}^-$ . Under what conditions can precipitation of  $\text{Zn}(\text{CN})_2(s)$  be avoided? To



answer this, we need EPAD that show the solid phases in zinc cyanide systems. Figures E-20 through E-23 are pL-pH EPAD like figure E-19, but they show the predominance areas for solid phases at the  $pM = pZn$  values specified in each EPAD. Figures E-20 through E-23 show that  $Zn(CN)_2(s)$  does not form (1) at any pH if pCN exceeds 4.1, i.e., free  $CN^-$  concentration below  $8 \times 10^{-5}M$  (2.1 ppm), or (2) if the pH exceeds 9.8, provided pZn is greater than 3.0, i.e., zinc concentration below  $1 \times 10^{-3}M$  (65 ppm).

Another look at the system is provided by figures E-11 through E-14, which show pM-pH EPAD for  $M = Zn(II)$  and specified values of  $pL = pCN$ . Figures E-11 through E-14 show that  $Zn(CN)_2(s)$  does not form at any pH or pCN value if pZn is above 4.5, i.e., zinc concentration below  $3 \times 10^{-5}M$  (2 ppm).

Can  $Zn(CN)_2(s)$  precipitation be avoided at pH 11? Problems involving constant pH are efficiently handled with pM-pL EPAD. The zinc cyanide system at pH 11 is diagramed in figure E-26. Figure E-26 shows that  $Zn(CN)_2(s)$  forms only at pZn below 0.4, i.e., zinc concentration above  $0.4M$  (about  $25 g \cdot L^{-1}$ ). At zinc concentrations usually encountered in practice, up to  $0.5 g \cdot L^{-1}$ ,  $Zn(CN)_2(s)$  will not precipitate. However,  $Zn(CN)_2(s)$  might precipitate from leach solutions allowed to evaporate or absorb  $CO_2$  with a resultant decrease of pH.

#### Example 6: Recovery of Zinc as Zinc Cyanide

Recovery of cyanide values from barren Merrill-Crowe cementation solutions may be of interest in connection with cyanide recycle. One way to recover  $CN^-$  or remove zinc is by precipitation as  $Zn(CN)_2(s)$ . Given a solution with total  $Zn = 0.002M = 130 \text{ ppm}$  ( $pZn = 2.7$ ), total  $CN^- = 0.009M = 230 \text{ ppm}$  ( $pCN = 2.05$ ), and pH 11.3, how much  $Zn^{2+}$  is required to recover Zn or  $CN^-$  as  $Zn(CN)_2(s)$ ? We require  $Zn^{2+}$  to precipitate the  $CN^-$  and to lower the pH by reacting with  $OH^-$  and precipitating  $ZnO(s)$  or  $Zn(OH)_2(s)$ . Total  $CN^- = 0.009M$  requires  $Zn^{2+} = (1/2) \times 0.009M = 0.0045M$  to convert all  $CN^-$  to  $Zn(CN)_2(s)$ . The pL-pH EPAD for pZn = 3.0 and 2.0, figures E-22 and E-23, show that precipitation of  $Zn(CN)_2(s)$  requires pH below about 10. At pH = 11.3,  $[H^+] = 5 \times 10^{-12}M$  and  $[OH^-] = K_w/[H^+] = (1 \times 10^{-14})M^2/[H^+] = 0.002M$ . So additional  $Zn^{2+} = (1/2) \times 0.002M = 0.001M$  is required to precipitate  $ZnO(s)$  or  $Zn(OH)_2(s)$  and lower the pH. Hence, the total zinc concentration needed is  $0.0045M + 0.001M = 0.0055M$ . With  $0.002M$  Zn already present, the  $Zn^{2+}$  needed is  $0.0055M - 0.002M = 0.0035M$ . After the calculated amount of  $Zn^{2+}$  is added, the system will contain a mixture of  $ZnO(s)$  and  $Zn(CN)_2(s)$ . Note that from the EPAD the predominance areas of  $Zn^{2+}$  and  $[Zn(CN)_4]^{2-}$  are separated

from each other by the predominance areas of other species, so mixing  $Zn^{2+}$  and  $[Zn(CN)_4]^{2-}$  will result in reaction as exemplified; see figures E-13 and E-14.

The EPAD can be used to estimate the composition of the supernatant solution to decide on its disposal. Figures E-21 through E-23 show that solutions with coexisting  $ZnO(s)$  and  $Zn(CN)_2(s)$  have  $pCN = 4.1$ , i.e., free  $CN^- = 8 \times 10^{-5}M$ , if pH is below 9.2. Figures E-11 and E-12, the pZn-pH diagrams for pCN = 5.0 and 4.0, show that the solubility of  $Zn(CN)_2(s)$  is  $pZn = 4.5$ , i.e.,  $Zn = 3 \times 10^{-5}M$  (2 ppm), if the pH is adjusted to about 8. The predominant solution species is  $Zn(CN)_2(aq)$ . Total  $CN^-$  is roughly  $8 \times 10^{-5} + 2(3 \times 10^{-5}) = 1.4 \times 10^{-4}M$  (3.6 ppm). This value of total  $CN^-$  may be high for immediate disposal, so treatment to remove  $CN^-$  may be required.

The recovered  $Zn(CN)_2(s)$  may be converted to HCN and ZnS by treatment with  $H_2S$ , for example.

#### Example 7: Decomposition of Zinc Cyanide Species

If recycle of cyanide is under consideration, the possibility of recovering cyanide as HCN may be of interest. From barren Merrill-Crowe solutions, what conditions are required to totally decompose zinc cyanide species to  $Zn^{2+}$  and recover HCN? The answer depends on the zinc concentration. Figures E-11 through E-14 and E-20 through E-23 confirm that  $Zn^{2+}$  predominates in sufficiently acidic solutions, so it is possible to totally decompose all zinc cyanide species. As acid is added, decomposition occurs and HCN is liberated, which raises pCN. Thus, the total cyanide concentration of the solution will be converted to free  $CN^-$ . Suppose the solution contains  $8 \times 10^{-3}M$  (210 ppm) total  $CN^-$  and  $1 \times 10^{-3}M$  (65 ppm) Zn, i.e., pZn = 3.0. Figure E-22 shows that at pZn = 3.0 and  $8 \times 10^{-3}M$  free  $CN^-$  ( $pCN = 2.1$ ), acidification to pH below 5.0 will decompose all zinc cyanide species, including  $Zn(CN)_2(s)$ .

#### Example 8: Mixed Metals in Cyanide Systems—Zinc and Iron

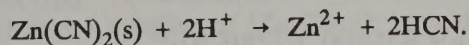
A disposal alternative for barren Merrill-Crowe solutions is addition of  $FeSO_4$  to complex cyanide as  $[Fe(CN)_6]^{4-}$  and precipitate it as  $Zn_2Fe(CN)_6$ . What happens when  $Fe^{2+}$  is added to a zinc-containing cyanide solution? To answer this question, figure 10-1 is useful. Consider a waste cyanide solution containing  $1 \times 10^{-4}M$  Zn (6.5 ppm, pZn = 4.0) and  $4.8 \times 10^{-3}M$  total  $CN^-$ , made  $1 \times 10^{-3}M$  in  $Fe^{2+}$  ( $pFe(II) = 3.0$ ) to complex the  $CN^-$ . What reaction products are expected? Figure 10-1 shows that the  $(\log K^*)/n$  lines for  $Fe(II)$  cyanide species are above the  $(\log K^*)/n$  lines for all zinc cyanide species, so thermodynamically  $Fe^{2+}$  is expected to remove  $CN^-$  from



all zinc cyanide species. Therefore, all  $\text{CN}^-$  is expected to be converted to  $(4.8 \times 10^{-3})/6 = 8 \times 10^{-4}M$  total dissolved and precipitated  $[\text{Fe}(\text{CN})_6]^{4-}$ . That leaves 0.001 - 0.0008 = 0.0002M  $\text{Fe}^{2+}$ , which will be precipitated by  $\text{OH}^-$  or  $[\text{Fe}(\text{CN})_6]^{4-}$ , depending on pH. The predominant species are determined by the solution pH and pCN. Given those values, the predominant zinc species are given by the zinc solution-species pCN-pH EPAD (figure E-19) and the corresponding EPAD for pZn = 4.0 (figure E-21). A pCN-pH EPAD for pZn = 4.0 with added  $[\text{Fe}(\text{CN})_6]^{4-}$  is also required; the EPAD for  $1 \times 10^{-4}M$   $[\text{Fe}(\text{CN})_6]^{4-}$  is shown in figure E-24. Figure E-24 shows that zinc is precipitated as  $\text{Zn}_2\text{Fe}(\text{CN})_6(\text{s})$  at pH below 8.8, and  $\text{ZnO}(\text{s})$  at pH above 8.8. At pH near 8 and pCN near 6, figure E-19 shows the predominant zinc solution species to be  $\text{Zn}^{2+}$ . Because  $[\text{Fe}(\text{CN})_6]^{4-}$  is kinetically inert (see chapter 8), it does not dissociate if the solution is diluted or acidified. If insufficient  $\text{Zn}^{2+}$  or  $\text{Fe}^{2+}$  is present to precipitate all of the  $[\text{Fe}(\text{CN})_6]^{4-}$ ,  $[\text{Fe}(\text{CN})_6]^{4-}$  will be the predominant iron solution species.

### Example 9: pZn-pH Diagrams

Sometimes there are problems for which the available EPAD may not give a quick solution because the solution composition data comprise values for which EPAD are not provided. This example and the next one show how this problem can be managed. Consider figures E-12 through E-14 and the  $\text{Zn}(\text{CN})_2(\text{s})$ - $\text{Zn}^{2+}$  equilibrium. That equilibrium is represented by the boundary between the  $\text{Zn}(\text{CN})_2(\text{s})$  and  $\text{Zn}^{2+}$  predominance areas. To generate the reaction equation, put the two zinc species on opposite sides. Insert successively the ligand species, HCN in this case, then  $\text{H}^+$  or  $\text{OH}^-$  to balance charges, then  $\text{H}_2\text{O}$  to balance H and O atoms. The result in this example is



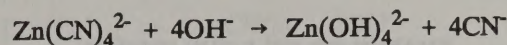
Log K for this reaction is given by

$$\log K = \log a(\text{Zn}^{2+}) + 2 \log a(\text{HCN}) - 2 \log a(\text{H}^+)$$

in accordance with equation 4-10. This equation shows that for every unit change of  $\log a(\text{HCN})$ ,  $\log a(\text{H}^+)$  = -pH changes by 1 unit. For example, the  $\text{Zn}(\text{CN})_2(\text{s})$ - $\text{Zn}^{2+}$  boundary shifts 2 pH units lower on going from figure E-12 with pCN = 4.0 to figure E-14 with pCN = 2.0. At pCN = 2.5 ( $[\text{CN}^-] = 0.003M$ ), the boundary occurs 0.5 pH unit higher than in figure E-14.

For another example, consider the equilibrium of  $\text{Zn}(\text{CN})_4^{2-}$  with  $\text{Zn}(\text{OH})_4^{2-}$ , which is represented by the boundary between the predominance areas for these

species in figure E-14. Proceeding as in the preceding paragraph, the reaction equation is



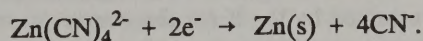
and the equilibrium expression is

$$\begin{aligned} \log K &= \log a(\text{Zn}(\text{OH})_4^{2-}) + 4 \log a(\text{CN}^-) \\ &\quad - \log a(\text{Zn}(\text{CN})_4^{2-}) - 4 \log a(\text{OH}^-). \end{aligned}$$

On the boundary, the activities of  $\text{Zn}(\text{CN})_4^{2-}$  and  $\text{Zn}(\text{OH})_4^{2-}$  are equal, and the log K equation shows that for every unit change of  $\log a(\text{OH}^-)$ , i.e., every unit change in pH,  $\log a(\text{CN}^-)$  changes by 1 unit. In figure E-14, drawn for pCN = 2.0, the boundary occurs at pH 13.0. At pCN = 1.5, the boundary would be at pH = 13.5, and at pCN = 3.0 it would be at pH = 12.0. The last instance corresponds to figure E-13, which however shows that  $\text{Zn}(\text{OH})_3^-$ , not  $\text{Zn}(\text{OH})_4^{2-}$ , predominates at pH = 12.0. This last illustration shows that this approach fails if the predominant species changes in the composition region of interest. If the user is operating with compositions bracketed by EPAD both above and below the values of interest, changes in predominant species can be easily noted. In cases such as this, the data in table D-2 also could be used to analyze the problem.

### Example 10: Reduction of Zinc in Cyanide Solutions

Conceivably one might consider electrolytic recovery of zinc from barren Merrill-Crowe solutions. Consider figure E-31, which is an Eh-pH diagram for pZn = 2.0 and pCN = 2.0, with regard to the reduction of  $\text{Zn}(\text{CN})_4^{2-}$  to zinc metal. Proceeding similarly to the preceding example, the reaction equation is



For redox half-reactions, the Nernst equation, equation 4-16, is used instead of equation 4-10:

$$E = E^\circ - (2.303RT/nF) \log Q,$$

where in this example

$$\log Q = 4 \log a(\text{CN}^-) - \log a(\text{Zn}(\text{CN})_4^{2-}).$$

The factor  $2.303RT/F$  is 0.05916 or approximately 0.06 V at 25° C; in this example  $n = 2$ , so  $(2.303RT/nF) = 0.03$  V. For every negative unit change in  $\log a(\text{Zn}(\text{CN})_4^{2-})$ , i.e., every tenfold decrease in  $a(\text{Zn}(\text{CN})_4^{2-})$ , E is lower



(more negative) by 0.03 V. Similarly, for every tenfold decrease in  $a(\text{CN}^-)$ ,  $E$  is higher (more positive) by  $4 \times 0.03 = 0.12$  V.

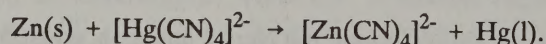
### EXAMPLES OF EQUILIBRIUM CONSTANT CALCULATIONS

Often calculation of an equilibrium constant is an effective way to get an answer to a practical mineral processing problem. In complex systems, several EPAD may be required to solve a problem, and a sufficient number of EPAD may not be available. Redox reactions for example, may require complex EPAD if more than one metal or ligand is present. The choice of whether to attack a problem with EPAD or by equilibrium-constant calculations may not be clear cut; it depends on the complexity of the chemical system and the needs and objectives at hand. For complex problems, the reader may prefer to employ some of the computerized procedures cited at the beginning of this chapter.

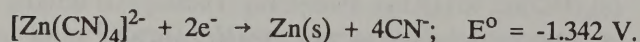
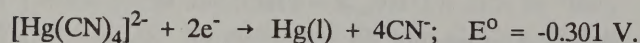
Equilibrium constants  $K$  for reactions of interest can be calculated from the thermodynamic data in appendixes B, C, and D. Tables 8-5 and 10-2, and figure 10-1, may also be used. The equations for these calculations are outlined in chapter 4. The value of  $K$  indicates the extent to which the reaction can go. It should be noted that whether the reaction will go is a matter of reaction rate. Information about rates of pertinent reactions is compiled in chapters 7 and 8. Solution of reaction rate problems is described in chapter 12.

#### Example 1: Cementation

Accessory metals may exist in precious metals leach solutions, and it is of interest to determine their behavior in a process. These accessory metals commonly exist in associated minerals, and they may be leached along with the precious metals. One such accessory metal is mercury. Can zinc cement mercury from cyanide solution? The answer is determined by  $\log K$  for the cementation reaction



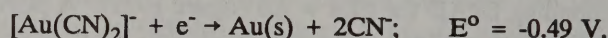
It is convenient to use the reduction half-reactions and their standard potentials in table 8-5:



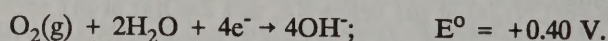
These data give  $E^\circ = +1.041$  V, hence  $\log K = +35.2$ , for the cementation reaction. Accordingly, zinc is expected to quantitatively cement mercury from cyanide solution.

#### Example 2: Gold Leaching

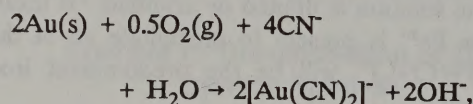
The reuse of barren cementation solutions for leaching would conserve reagents and might lower disposal costs. Barren Merrill-Crowe solutions contain zinc, but it may still be possible to recycle such solutions to leaching. Could a  $\text{Zn}(\text{CN})_4^{2-}$  solution be used to leach gold? From table 8-5:



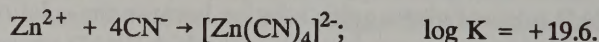
From  $\Delta_r G^\circ$  data in table C-1:



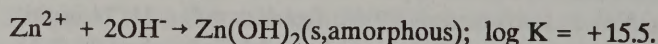
The net reaction is



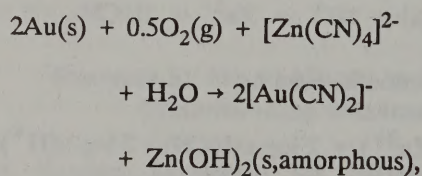
for which  $E^\circ = +0.89$  V, hence  $\log K = +30.1$ . For  $[\text{Zn}(\text{CN})_4]^{2-}$  as the cyanide source, we need its  $\log K$  data from table D-2:



The zinc-containing product is expected to be  $\text{Zn}(\text{OH})_2$  (s,amorphous) or  $[\text{Zn}(\text{OH})_4]^{2-}$ . At pH 11, the EPAD for zinc in cyanide systems, e.g., figures E-13 and E-14, show precipitation of  $\text{ZnO(s)}$  [or  $\text{Zn}(\text{OH})_2$  (s,amorphous)]. For its formation (table D-2),



The expected leaching reaction is then

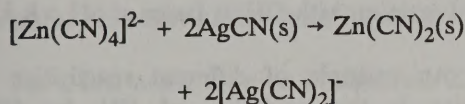


for which  $\log K$  is  $(+30.1) - (+19.6) + (+15.5) = +26.0$ . This is only 4.1  $\log K$  units less positive than for the reaction with free  $\text{CN}^-$ , so leaching gold with  $[\text{Zn}(\text{CN})_4]^{2-}$  solution is thermodynamically feasible. Therefore, it is appropriate to determine whether the rate of this reaction is satisfactory, and to what extent the precipitated  $\text{Zn}(\text{OH})_2$  hinders it.

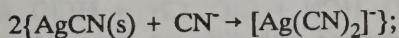


### Example 3: Silver Versus Zinc Cyanide Species

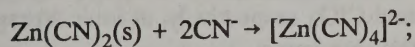
If barren Merrill-Crowe solutions could be used to leach gold, would they be as effective for leaching silver? In the case of silver, the extent to which AgCN might precipitate and hinder recovery is of concern. Can AgCN(s) dissolve in  $[\text{Zn}(\text{CN})_4]^{2-}$  solutions? For this mixed-metals problem, table 10-2 and figure 10-1 are convenient. Figure 10-1 shows that the answer is yes because the AgCN(s)- $[\text{Ag}(\text{CN})_2]^-$  line corresponds to larger values of  $(\log K^*)/n$  than does the  $\text{Zn}(\text{CN})_2(\text{s})$ - $[\text{Zn}(\text{CN})_4]^{2-}$  line. Similarly, in tables 10-2 and 10-3, the reaction obtained by subtracting a reaction with a low value of  $(\log K)/n$  or  $(\log K^*)/n$  from a reaction with a high value of  $(\log K)/n$  or  $(\log K^*)/n$  is expected to proceed. The calculation of  $\log K$  for the reaction



follows. The reactions for the silver and zinc species separately are first given.



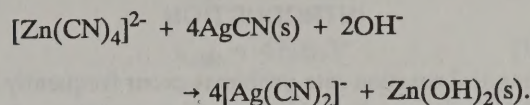
$$n = 1, (\log K)/n = +4.8.$$



$$n = 2, (\log K)/n = +2.0.$$

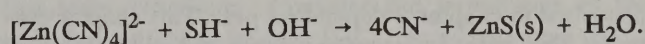
For the reaction of interest,  $\log K$  is obtained by multiplying the  $(\log K)/n$  values by the  $n$ 's and the reaction multipliers (2 and 1, respectively) and subtracting:  $\log K = (+4.8)(1)(2) - (+2.0)(2)(1) = +5.6$ . Hence, stirring AgCN(s) into a solution of  $[\text{Zn}(\text{CN})_4]^{2-}$  is predicted to result in dissolution of AgCN(s) and precipitation of  $\text{Zn}(\text{CN})_2(\text{s})$ . Conversely, silver is predicted to remain dissolved in a solution containing  $[\text{Zn}(\text{CN})_4]^{2-}$ , and such a solution should be satisfactory for leaching silver. This calculation is applicable to solutions with pH 9 to 10, where  $\text{Zn}(\text{CN})_2(\text{s})$  is a stable phase. At pH 11 or higher, the stable solid phase is ZnO or  $\text{Zn}(\text{OH})_2(\text{s})$ . A calculation similar to that above with  $\text{Zn}(\text{OH})_2(\text{s})$  as the product

leads to a similar conclusion; the reaction shows that high pH favors dissolution of AgCN(s):



### Example 4: Regeneration of Cyanide From Zinc-Containing Solutions

If recycle of cyanide solutions is of interest, sulfide precipitation offers a means of regenerating free  $\text{CN}^-$  from zinc-containing solutions, via the reaction



From the thermodynamic data in tables B-1, C-1, and D-2,  $\log K$  for this reaction is calculated as +5.8. For converting 0.01M total cyanide in the form of  $[\text{Zn}(\text{CN})_4]^{2-}$  to free  $\text{CN}^-$  at pH 11, this reaction is therefore feasible.

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## CHAPTER 12.—SOLUTION OF REACTION RATE PROBLEMS

### INTRODUCTION

Chemical reaction rate problems occur frequently in industrial processes. It is often necessary to determine the extent of a reaction during a given time, or to determine how much time is required for a desired conversion. Most chemical reactions are first or second order with respect to substrate or reagent, as outlined in chapter 7, which reviews the reactions of free  $\text{CN}^-$  and derived species such as formamide ( $\text{H}-\text{CO}-\text{NH}_2$ ), cyanogen chloride ( $\text{ClCN}$ ), and cyanate ( $\text{NCO}^-$ ). As a rule, the rates of the reactions described in chapter 7 depend on pH. This chapter continues first with a discussion of the pH dependence of chemical reaction rates. The two following sections review first-order and second-order rate equations and provide the mathematical formulas useful for solving practical problems. For both kinds of rate equations, examples of their application to problems of interest in precious metals hydrometallurgy are given. Finally, the calculation of rate constants at different temperatures is discussed.

### DEPENDENCE OF REACTION RATES ON pH

As a rule, the rates of chemical reactions in aqueous solution depend on pH. The nature of the pH dependence of reaction rates for a given reaction must be determined experimentally. Two major reasons that reaction rates depend on pH are the following:

- The reactants are weak acids or bases that form different species as a function of pH. These species differ in their reactivities. The species thus formed are characterized by  $\text{pK}_a$  values between 0 and 14, and appear on equilibrium predominance area diagrams (EPAD). Examples are  $\text{HCN} \rightarrow \text{CN}^- + \text{H}^+$  with  $\text{pK}_a = 9.2$  and  $\text{HClO} \rightarrow \text{ClO}^- + \text{H}^+$  with  $\text{pK}_a = 7.5$  at  $25^\circ\text{C}$ . There are often cases in which the most reactive species is a very strong acid with  $\text{pK}_a < 0$  or is derived from a very weak acid with  $\text{pK}_a > 14$ , and does not appear on EPAD at pH 0 to 14.

- A reactant, even one that does not have observable acid-base equilibria, reacts with the species  $\text{H}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{OH}^-$  at different rates.

The rate constants for the reactions of the different species of reactants often differ by many powers of 10; consequently, at a given pH, the reactive species is not always the predominant species that appears on EPAD.

EPAD are based solely on thermodynamic data and say nothing about reaction rates.

*Example:* An example of different reactivities of a substrate with  $\text{H}_2\text{O}$  and  $\text{OH}^-$  is the hydrolysis of  $\text{ClCN}$ . This reaction proceeds with a rate equation

$$-d[\text{ClCN}]/dt = k[\text{ClCN}], \quad (12-1)$$

$$\text{where } k = (k_a + k_b[\text{OH}^-]) \quad (12-2)$$

from table F-9 in appendix F. The  $k_a$  and  $k_b$  terms represent the reaction rates of  $\text{ClCN}$  with  $\text{H}_2\text{O}$  and  $\text{OH}^-$ , respectively. At  $25^\circ\text{C}$ ,  $k_a = 4.9 \times 10^{-7} \text{ s}^{-1}$  and  $k_b = 12.2 (\text{mol} \cdot \text{L}^{-1})^{-1} \text{ s}^{-1}$ . As shown by calculation and in figure 7-19, reaction with  $\text{H}_2\text{O}$  is faster at  $\text{pH} < 6$ , i.e.,  $k_a > k_b[\text{OH}^-]$ ; and reaction with  $\text{OH}^-$  is faster at  $\text{pH} > 8$ , i.e.,  $k_b[\text{OH}^-] > k_a$ .

*Example:* An example of different reactivities of reactant species is the oxidation of  $\text{CN}^-$  by  $\text{ClO}^-$  (hypochlorite). In this reaction,  $\text{CN}^-$  and  $\text{HCN}$  (hydrocyanic acid) each react at different rates with each of the oxidant species  $\text{ClO}^-$  and  $\text{HClO}$ . The elementary reactions  $\text{HCN} + \text{HClO}$ ,  $\text{HCN} + \text{ClO}^-$ ,  $\text{CN}^- + \text{HClO}$ , and  $\text{CN}^- + \text{ClO}^-$  each proceed with different rate constants. As described in chapter 7, published observations showed that at pH 12 to 14, where free cyanide and hypochlorite are nearly all  $\text{CN}^-$  and  $\text{ClO}^-$ , respectively, at ionic strength 1.00M and  $25^\circ\text{C}$ , the rate law is

$$-d[\text{CN}^-]/dt = (k_1 + k'_2[\text{OH}^-]^1)[\text{CN}^-][\text{ClO}^-], \quad (12-3)$$

$$\text{where } k_1 = 310 (\text{mol} \cdot \text{L}^{-1})^{-1} \cdot \text{s}^{-1}$$

$$\text{and } k'_2 = 583 \text{ s}^{-1}.$$

Alternatively, the  $k'_2$  term may be expressed as a  $[\text{H}^+]$  dependence:

$$-d[\text{CN}^-]/dt = (k_1 + k_2[\text{H}^+])[\text{CN}^-][\text{ClO}^-], \quad (12-4)$$

$$\text{where } k_2 = k'_2 K_w^{-1}, \quad (12-5)$$

$$\text{and } K_w = [\text{H}^+][\text{OH}^-]. \quad (12-6)$$

At ionic strength 1.00M and  $25^\circ\text{C}$ ,  $\log K_w = -13.79$  from table C-2, so equation 12-5 gives  $k_2 = 3.6 \times 10^{16} (\text{mol} \cdot \text{L}^{-1})^2 \cdot \text{s}^{-1}$ . The  $k_2$  term in equation 12-4 was interpreted as an elementary reaction of  $\text{CN}^-$  with  $\text{HClO}$ , in which  $\text{Cl}^+$  is transferred from  $\text{HOCl}$  to  $\text{CN}^-$  to form



CICN, which is the observed product. The  $k_1$  and  $k_2$  terms of equation 12-4 are accordingly equal at pH about 13.9. Although the  $pK_a$  of HClO is 7.5 from table C-2, so that  $\text{ClO}^-$  is the predominant oxidant species at pH 12 to 13.9, HClO is more reactive than  $\text{ClO}^-$  with  $\text{CN}^-$  in this pH range.

## FIRST-ORDER REACTIONS

This section reviews first-order reactions and provides the general mathematical equations into which the user can insert pertinent data to obtain solutions to practical problems. Hydrolysis reactions of free  $\text{CN}^-$  and derived species are first-order in substrate; for these reactions, the rate constant varies with pH. At a given constant pH, hydrolysis reactions may be treated as first-order reactions and treated as described in this section.

### General Solution of the Rate Equation

For a first-order reaction of substrate Z,



the rate equation is

$$d[\text{Z}]/dt = -k'[\text{Z}], \quad (12-8)$$

where  $[\text{Z}]$  = concentration of Z,

and  $t$  = time.

The first-order rate constant  $k'$  has units of (time)<sup>-1</sup>. Integration gives

$$[\text{Z}] = [\text{Z}]_0 \exp(-k't), \quad (12-9)$$

where  $[\text{Z}]_0$  = concentration of Z at zero time.

The fraction of Z reacted,  $f_z$ , is

$$f_z = ([\text{Z}]_0 - [\text{Z}])/[\text{Z}]_0 = 1 - \exp(-k't). \quad (12-10)$$

The time  $t_f$  required to attain conversion  $f_z$  is

$$t_f = -(k')^{-1} \ln(1 - f_z) \quad (12-11)$$

and is independent of the concentration of Z. The times required for 50-, 90-, and 99-pct conversion are then, respectively,

$$t_{0.50} = 0.693/k', \quad (12-12)$$

$$t_{0.90} = 2.303/k', \quad (12-13)$$

and

$$t_{0.99} = 4.605/k'. \quad (12-14)$$

Equations 12-10 and 12-11 are the most pertinent to solving practical problems; equations 12-12 through 12-14 are special cases of equation 12-11.

### Examples

As described in chapter 7, hydrolysis reactions are first order in substrate and at a given pH may be treated as first-order reactions. Consider the importance of the hydrolysis of  $\text{CN}^-$  to formate ( $\text{HCO}_2^-$ ) and ammonia ( $\text{NH}_3$ ) for cyanide degradation at 25° C and pH 11.0. From table F-3, the rate equation for hydrolysis of  $\text{CN}^-$  is

$$d[\text{CN}^-]/dt = -k'([\text{CN}^-] + [\text{HCN}]), \quad (12-15)$$

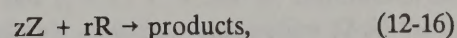
in which  $k' = 1.01 \times 10^{-8} \text{ s}^{-1}$ . From equations 12-12 through 12-14, the times for 50-, 90-, and 99-pct reaction of cyanide by equation 12-15 are  $0.69 \times 10^8 \text{ s} = 2.2 \text{ years}$ ;  $2.3 \times 10^8 \text{ s} = 7.2 \text{ years}$ ; and  $4.6 \times 10^8 \text{ s} = 14 \text{ years}$ , respectively. The rate of this reaction is so slow that it may not be a major pathway for cyanide degradation. These calculations are based on the uncatalyzed reaction; no information is available concerning catalysis of this reaction.

## SECOND-ORDER REACTIONS

This section reviews second-order reactions and provides the general mathematical equations into which the user can insert pertinent data to obtain solutions to practical problems. The most important practical examples of second-order reactions are the reactions of  $\text{CN}^-$  and derived species with oxidants. The rates of these reactions also depend on pH. At a given constant pH, redox reactions may be treated as second-order reactions and treated as described in this section.

### General Solution of the Rate Equation

For a second-order reaction of  $z$  moles of substrate Z with  $r$  moles of reagent R,





the rate equation is

$$z^{-1}d[Z]/dt = r^{-1}d[R]/dt = -k''[Z][R]. \quad (12-17)$$

The second-order rate constant  $k''$  has units of (concentration)<sup>-1</sup> times (time)<sup>-1</sup>.

For the special case of Z and R present in stoichiometric ratio, i.e.,  $[Z]/z = [R]/r$ , integration gives

$$[Z]/[Z]_0 = [R]/[R]_0 = (1 + r[Z]_0 k'' t)^{-1}, \quad (12-18)$$

where  $[Z]_0$  and  $[R]_0$  are the respective concentrations of Z and R at zero time. The conversion  $f_Z$  and the fraction of reagent consumed  $f_R$  are

$$f_Z = f_R = r[Z]_0 k'' t (1 + r[Z]_0 k'' t)^{-1}. \quad (12-19)$$

The time  $t_f$  for a given degree of conversion depends on the initial concentration of Z,

$$t_f = f_Z (1 - f_Z)^{-1} (r[Z]_0 k'')^{-1}. \quad (12-20)$$

For 50-, 90-, and 99-pct conversion of Z,

$$t_{0.50} = 1/r[Z]_0 k'', \quad (12-21)$$

$$t_{0.90} = 9/r[Z]_0 k'', \quad (12-22)$$

$$t_{0.99} = 99/r[Z]_0 k''. \quad (12-23)$$

Equations 12-19 and 12-20 are the most pertinent to solving practical problems; equations 12-21 through 12-23 are special cases of equation 12-20.

For the general case with excess reagent such as an oxidant, integration of equation 12-10 gives, with Q defined as  $z[R]_0 - r[Z]_0$ ,

$$\begin{aligned} [Z]/[Z]_0 &= Q [\exp(-Qk''t)] \\ &\times \{z[R]_0 - r[Z]_0 \exp(-Qk''t)\}^{-1}, \end{aligned} \quad (12-24)$$

$$[R]/[R]_0 = Q / \{z[R]_0 - r[Z]_0 \exp(-Qk''t)\} \quad (12-25)$$

The fractional conversion  $f_Z$  of Z is

$$\begin{aligned} f_Z &= [1 - \exp(-Qk''t)] \\ &/ \{1 - (r/z)([Z]_0/[R]_0) \exp(-Qk''t)\}. \end{aligned} \quad (12-26)$$

The time  $t_f$  required to attain conversion  $f_Z$  is

$$\begin{aligned} t_f &= (Qk'')^{-1} \\ &\times \ln \{[1 - (r/z)([Z]_0/[R]_0)f_Z]/(1 - f_Z)\}. \end{aligned} \quad (12-27)$$

Equations 12-24 through 12-27 are the equations useful for solving practical problems.

For the case with R in very large excess over Z, equations 12-24, 12-26, and 12-27 become, approximately,

$$[Z]/[Z]_0 = \exp(-z[R]_0 k'' t), \quad (12-28)$$

$$f_Z = 1 - \exp(-z[R]_0 k'' t), \quad (12-29)$$

$$t_f = -(z[R]_0 k'')^{-1} \ln(1 - f_Z). \quad (12-30)$$

Equations 12-28 through 12-30 are equivalent to equations 12-9 through 12-11 with  $k'$  replaced by  $z[R]_0 k''$ . Accordingly, the kinetics of a second-order reaction with reagent in very large excess over substrate is termed "pseudo-first-order." This pseudo-first-order behavior also occurs if  $[R]$  is maintained constant, e.g., by metering it into a reactor or by a solubility equilibrium. An example of the latter is the constant concentration of dissolved  $O_2$  during oxygen oxidations in the presence of excess air. Note that equations 12-29 and 12-30, like equations 12-10 and 12-11, are independent of the concentration of the substrate Z. Equations 12-28 through 12-30 are the equations applicable to solving practical problems.

The times  $t_f$  required for a given conversion  $f_Z$  of Z decrease with the increase of the initial reagent-substrate ratio  $[R]_0/[Z]_0$ , the more rapidly for high  $f_Z$ . This is shown in the following tabulation, which gives relative values of  $t_f$ , namely  $[R]_0 k'' t_f$ , for the case of R and Z reacting in 1:1 mole ratio, namely  $r = z$ , calculated by means of equations 12-20 and 12-27:

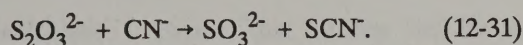
		$[R]_0 k'' t_f$ for $f_Z =$			
$R_0/Z_0$		0.5	0.9	0.99	0.999
1.0	1.000	9.00	99.0	999.0	
1.1	.957	6.58	25.3	49.7	
1.2	.925	5.50	17.17	30.7	
1.5	.863	4.16	10.58	17.43	
2.0	.811	3.41	7.84	12.43	
5.0	.735	2.63	5.48	8.36	
10.0	.713	2.45	5.00	7.56	
Infinite	.693	2.30	4.61	6.91	



The first row of the table gives  $[R]_0 k'' t_f$  for reagent and substrate in stoichiometric ratio (equation 12-20). The last row gives  $[R]_0 k'' t_f$  for reagent in huge excess over substrate, i.e., pseudo-first-order conditions.

### Example

In mineral process solutions, thiosulfate ( $S_2O_3^{2-}$ ) is often present when the solutions have contacted sulfide minerals. As described in chapter 7,  $S_2O_3^{2-}$  reacts with  $CN^-$  to form thiocyanate ( $SCN^-$ ). Accordingly, one may ask at what rate  $S_2O_3^{2-}$  converts  $CN^-$  to the less toxic  $SCN^-$ . A slow rate for this reaction would make it an impractical method for cyanide detoxification, but a rapid rate would require increased cyanide makeup for leaching. The reaction is



The reagent  $S_2O_3^{2-}$  reacts with the substrate  $CN^-$  in 1:1 mole ratio, so  $r = z = 1$ . From table F-1, the rate equation is

$$d[CN^-]/dt = -k''[S_2O_3^{2-}][CN^-] \quad (12-32)$$

at  $pH > 11$ , where free cyanide is nearly all  $CN^-$ . At  $25^\circ C$ ,  $k'' = 1.2 \times 10^{-5} (\text{mol} \cdot \text{L}^{-1})^{-1} \cdot \text{s}^{-1}$  from table F-1. For initial  $[Z]_0 = [CN^-]_0 = 0.010M$  and  $[R]_0 = [S_2O_3^{2-}]_0 = 0.010M$ , equations 12-21 through 12-23 give the times for 50-, 90-, and 99-pct reaction as  $8.3 \times 10^6 \text{ s} = 96 \text{ days}$ ,  $7.5 \times 10^7 \text{ s} = 2.4 \text{ years}$ , and  $8.2 \times 10^8 \text{ s} = 26 \text{ years}$ , respectively. Under these conditions, the rate of this reaction is far too slow for practical detoxification of free  $CN^-$ . However, these results confirm that  $S_2O_3^{2-}$  is not expected to interfere with leaching operations by robbing  $CN^-$ . Alternatively, consider the behavior if  $S_2O_3^{2-}$  is held constant at  $0.010M$  by metering it into the solution. In that case, pseudo-first-order behavior occurs. Then equation 12-30 gives the times for 50-, 90-, and 99-pct conversion of  $CN^-$  as  $5.8 \times 10^6 \text{ s} = 67 \text{ days}$ ,  $1.92 \times 10^7 \text{ s} = 222 \text{ days}$ , and  $3.8 \times 10^7 \text{ s} = 1.2 \text{ years}$ , respectively. These conversion times are shorter than in the case without metered reagent and are the same for any value of the initial  $CN^-$  concentration. Again, reaction 12-31 is not practical for cyanide detoxification, but it would not rob  $CN^-$  from leaching operations. However, the  $S_2O_3^{2-}$ - $CN^-$  reaction is known to be catalyzed by copper species; in the absence of data, the effect of copper species on this reaction and on the conclusions just drawn is unknown.

### EFFECT OF TEMPERATURE ON REACTION RATES

The rates of chemical reactions vary greatly with temperature. A rough rule of thumb is that reaction rates

double for a  $10^\circ C$  rise in temperature. The relationship of reaction rate constant to temperature and activation parameters was discussed in chapter 7. Experimentally, data for rate constant  $k$  versus absolute temperature  $T$  usually fit an equation

$$\log k = A - BT^{-1}, \quad (12-33)$$

where  $A$  and  $B$  are empirically determined constants. The tables in appendix F present data for rate constants versus temperature for several reactions of free cyanide and derived species. For data at two temperatures, equation 12-33 is written for both temperatures  $T_1$  and  $T_2$ , and these two equations are combined:

$$\log (k_2/k_1) = B(T_1^{-1} - T_2^{-1}). \quad (12-34)$$

If equation 12-34 is rewritten for a data point at a third temperature, an equation for data at a third temperature can be obtained in terms of data at two other temperatures:

$$\begin{aligned} \log (k_3/k_1) &= \log (k_2/k_1) \\ &\times (T_1^{-1} - T_3^{-1}) / (T_1^{-1} - T_2^{-1}). \end{aligned} \quad (12-35)$$

Often data are available at two or more temperatures, so equation 12-35 is useful for calculating rate constants at other temperatures. If the temperature for which a rate constant is needed lies within or not far outside the temperature range of the available data, the uncertainty of the calculated rate constant is about the same as the uncertainty of the data. However, a rate constant calculated at a temperature much more than 10 pct outside the temperature range of the available data will be more uncertain than the experimental data employed.

### Example

Cyanogen chloride is formed when  $CN^-$  reacts with  $ClO^-$ . The  $ClCN$  hydrolyzes to  $NCO^-$  at a rate that increases with  $pH$ , as discussed above in connection with the effect of  $pH$  on reaction rate. The data are compiled in table F-9. The rate equations are equations 12-1 and 12-2. At  $25^\circ C$  ( $77^\circ F$ ),  $k_a = 4.9 \times 10^{-7} \text{ s}^{-1}$  and  $k_b = 12.2 (\text{mol L}^{-1})^{-1} \text{ s}^{-1}$ . At  $0^\circ C$  ( $32^\circ F$ ),  $k_a = 2.0 \times 10^{-8} \text{ s}^{-1}$  and  $k_b = 0.47 (\text{mol L}^{-1})^{-1} \text{ s}^{-1}$ . Calculate the rate constants at  $15^\circ C$  ( $59^\circ F$ ). The temperature variations of  $k_1$  and  $k_2$  differ, so the calculation must be done for each individually. Let  $T_1 = 25^\circ C = 298 \text{ K}$ ,  $T_2 = 0^\circ C = 273 \text{ K}$ , and  $T_3 = 15^\circ C = 288 \text{ K}$ . Insertion of the temperatures and rate constants in equation 12-35 for  $k_a$  and  $k_b$  respectively gives at  $15^\circ C$ ,  $k_a = 1.46 \times 10^{-7} \text{ s}^{-1}$  and  $k_b = 3.5 (\text{mol} \cdot \text{L}^{-1})^{-1} \cdot \text{s}^{-1}$ .



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## GLOSSARY

**Absorbance:** Amount of light absorption by a sample measured in a spectrophotometer. The absorbance  $A$  is related to the fraction of light transmitted  $T$  by  $A = -\log T$ . Dimensionless.

**Activation parameters:** The quantities activation energy, enthalpy, and entropy, which characterize the temperature dependence of the rate of a chemical reaction.

**Activity:** Thermodynamically effective concentration of a chemical species in a solution, related to the analytical concentration by an activity coefficient according to equation 4-24 in chapter 4. Dimensions: concentration.

**Activity coefficient:** Factor that relates activity to concentration. See **Activity**. Dimensionless.

**Addition reaction:** Chemical reaction in which two or more chemical species combine to form one chemical species. An example is  $\text{H}_2\text{NCN} + \text{H}_2\text{O} \rightarrow \text{CO}(\text{NH}_2)_2$ .

**Band, absorption:** Range of wavelengths of light absorbed by a chemical species.

**Complexed cyanide:** Cyanide bound to metal ions. Examples:  $\text{Hg}(\text{CN})_2$ ,  $[\text{Cu}(\text{CN})_3]^{2-}$ .

**Condensation reaction:** Chemical reaction in which two reactant species combine, often with elimination of another species. An example is  $2\text{Fe}(\text{CN})_5(\text{H}_2\text{O})^{3-} \rightarrow \text{Fe}_2(\text{CN})_{10}^{6-} + 2\text{H}_2\text{O}$ .

**Conjugate acid:** Chemical species derived from another chemical species by addition of a hydrogen ion. For example,  $\text{HCN}$  is the conjugate acid of  $\text{CN}^-$ ;  $\text{HCO}_3^-$  is the conjugate acid of  $\text{CO}_3^{2-}$ .

**Conjugate base:** Chemical species derived from another chemical species by removal of a hydrogen ion. For example,  $\text{CN}^-$  is the conjugate base of  $\text{HCN}$ ;  $\text{CO}_3^{2-}$  is the conjugate base of  $\text{HCO}_3^-$ .

**Coordination number:** Number of ligands bound to a central atom, usually a metal ion.

**Dinuclear:** Refers to metal species that contain two metal ions per molecule or ion. An example is  $\text{Fe}_2(\text{CN})_{11}^{6-}$ .

**Disproportionation reaction:** Redox chemical reaction in which a chemical species containing an element in one oxidation state reacts with itself to form products which contain that element in two different oxidation states.

**Eh:** Reduction potential relative to the standard potential for the half-reaction  $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$  defined as exactly zero.

**Eh-pH diagram:** An equilibrium predominance area diagram that shows predominant chemical species as a function of Eh and pH.

**Elementary reactions or steps:** Simple reactions involving usually one or two molecules or ions at a time that occur during a chemical reaction and constitute the mechanism of that reaction. See chapter 7.

**Elimination reaction:** Chemical reaction in which a chemical species decomposes into a related chemical species and a small molecule or ion. An example is  $\text{H}_2\text{NCOS}^- \rightarrow \text{NCO}^- + \text{H}_2\text{S}$ .

**EPAD (equilibrium predominance area diagrams):** Diagrams that show predominant chemical species in a system on the basis of equilibrium data, as a function of variables such as pH, pM, pL, or Eh. See chapter 4.

**Equilibrium constant:** Constant that relates the activities of chemical species in a reaction at equilibrium, defined in equation 4-10 in chapter 4.

**Exchange reaction:** Chemical reaction in which chemical species exchange groups of atoms. An example is  $\text{CH}_3\text{COSH} + \text{NH}_3 \rightarrow \text{CH}_3\text{CONH}_2 + \text{H}_2\text{S}$ .

**Excitation:** Elevation of a chemical species to a higher energy state.

**Excited state:** Energy state higher than the ground state of a chemical species. In photochemistry, electrons in a chemical species absorb light and are excited to a higher energy level, and the species is then in an electronic excited state.

**Free cyanide:** Cyanide not complexed with metal ions.

**Ground state:** State of lowest energy of a chemical species.

**Induction period:** Period of time elapsed from mixing of reactants to onset of reaction.

**Infrared light:** Light of wavelength from 700 nm = 0.7  $\mu\text{m}$  up to about 1,000  $\mu\text{m}$ .



**Ionic strength:** Half the sum of the products of the concentrations times the squared charges of all ions in a solution. See appendix A.

**Kinetics:** Chemical reaction rates.

**Labile:** Chemically reactive.

**Ligand:** Any chemical species that complexes with a metal ion.

**Mmaximum allowable concentration:** Maximum concentration of a toxic substance to which workers may be continually exposed without harm for a specified time, often 8 h.

**Molar absorptivity:** Measure of light absorption by a chemical species. It is related to the absorbance, the sample concentration, and the sample thickness by the Lambert-Beer law, equation 5-1. Dimensions: reciprocal concentration times reciprocal length.

**Mononuclear:** Refers to metal species that contain one metal ion per molecule or ion.

**Non-WAD:** Refers to metal cyanide species that are not decomposed by acids at pH 2 to 7 with liberation of HCN. See WAD.

**Order of a chemical reaction:** Dependence of a reaction rate on the concentrations of reacting species. See chapter 7.

**Partially WAD:** Refers to metal cyanide species that are partially decomposed by acids at pH 2 to 7 with liberation of HCN. See WAD.

**pH:**  $-\log a(\text{H}^+)$ , where  $a(\text{H}^+)$  is the activity of hydrogen ion,  $\text{H}^+$ .

**Photochemical reaction:** Chemical reaction caused to occur by absorption of light. See chapter 9.

**Photon:** Smallest unit, "particle," or quantum of light energy.

**pK:**  $-\log K$ , where  $K$  is an equilibrium constant. Often used for acid dissociation constants.

**pL:**  $-\log a(\text{L})$ , where  $a(\text{L})$  is the total activity of all free ligand species.

**pM:**  $-\log a(\text{M})$ , where  $a(\text{M})$  is the total activity of all metal species.

**pM-pH diagram:** An EPAD showing predominant chemical species as a function of pM and pH.

**pM-pL diagram:** An EPAD showing predominant chemical species as a function of pM and pL.

**Polynuclear:** Refers to metal species that contain more than one metal ion per molecule or complex ion. An example is  $\text{Cr}_3(\text{OH})^{45+}$ .

**Polyprotic:** Refers to acids or bases that can lose or gain more than one hydrogen ion,  $\text{H}^+$ . Examples are the acid  $\text{H}_3\text{PO}_4$  or the base  $[\text{Co}(\text{NH}_3)_4(\text{OH})_2]^{1+}$ .

**Quantum efficiency or yield:** Number of moles of photochemical reaction product per mole of absorbed photons.

**Rate constant:** Empirically determined numerical coefficients in a rate equation. Dimensions: (concentration) $^{-n+1}$  times (time) $^{-1}$ , where  $n$  is the total order of the reaction.

**Rate equation or rate law:** Mathematical equation that expresses how the rate of a chemical reaction depends on the concentrations of the involved chemical species.

**Rate-limiting or rate-determining step:** Elementary step of a chemical reaction that determines its rate.

**Standard state:** State of a chemical species to which its thermodynamic properties are referred. See chapter 4.

**Substitution reaction:** Chemical reaction in which a group of atoms in one reactant species substitutes for a group of atoms in another reactant species. An example is  $\text{ClCN} + \text{I}^- \rightarrow \text{ICN} + \text{Cl}^-$ .

**Substrate:** Reactant of primary interest, the other reactant(s) being reagent(s).

**Thermal reaction:** Chemical reaction that occurs only by thermodynamic driving force, as opposed to a photochemical reaction.

**Ultraviolet light:** Light of wavelength from 400 nm to about 10 nm. The atmospheric ozone layer cuts off solar ultraviolet light of wavelength shorter than 300 nm. Water and oxygen absorb at wavelengths below 200 nm.

**Visible light:** Light of wavelength 800 nm (red) to 400 nm (violet).

**WAD (weak-acid dissociable):** Refers to metal cyanide species that are completely decomposed by acids at pH 2 to 7 with liberation of HCN.



## APPENDIX A.—IONIC STRENGTH

Ionic strength was mentioned in chapter 4 in connection with equilibrium constants in solutions. In this appendix, ionic strength is defined, and its effects on chemical equilibria and reaction rates are outlined.

Ionic strength  $I$  is defined as

$$I = (1/2) \sum_i^n c_i z_i^2, \quad (\text{A-1})$$

where  $c_i$  and  $z_i$  are respectively, the concentration and ion charge of the  $i$ th species in the solution. The concentrations  $c_i$  may be moles per liter solution (molarity) or moles per kilogram solvent (molality). For a solution of one binary salt, the right-hand side of equation A-1 contains only two terms, i.e.,  $n = 2$ , and  $I$  is an integer multiple of the salt concentration  $c$ . Some examples are tabulated:

Electrolyte type	Example	$I/c$
1:1	NaCl	1
2:1 or 1:2	Na <sub>2</sub> SO <sub>4</sub> or CaCl <sub>2</sub>	3
3:1 or 1:3	Na <sub>3</sub> [Fe(CN) <sub>6</sub> ] or AlCl <sub>3</sub>	6
4:1 or 1:4	Na <sub>4</sub> [Fe(CN) <sub>6</sub> ] or ThCl <sub>4</sub>	10
2:2	MgSO <sub>4</sub>	4
3:2 or 2:3	Ca <sub>3</sub> [Fe(CN) <sub>6</sub> ] <sub>2</sub> or Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	15
4:2 or 2:4	Mg <sub>2</sub> [Fe(CN) <sub>6</sub> ] or Th(SO <sub>4</sub> ) <sub>2</sub>	12

Activity and activity coefficients were discussed in chapter 4. Activity  $a$ , activity coefficient  $\gamma$ , and concentration  $c$  are related by

$$a = \gamma c. \quad (\text{A-2})$$

The activity coefficient of an electrolyte varies strongly with concentration. By convention,  $\gamma$  is equal to 1 at infinite dilution, i.e.,  $c \rightarrow 0$ . With increasing concentration, hence ionic strength,  $\gamma$  decreases to a minimum, then increases rapidly. In very dilute solutions, the variation of  $\gamma$  with  $I$  is given approximately by

$$\log \gamma = -Az_+z_-I^{1/2} / (1 + I^{1/2}). \quad (\text{A-3})$$

Equation A-3 is the Debye-Hueckel limiting law for electrolyte activity coefficients. The quantity  $A$  is a solvent- and temperature-dependent constant. For water at 25° C,  $A$  is 0.511. The  $z$ 's are the ion charges. For further details, the reader is referred to textbooks on thermodynamics.

The effect of ionic strength on equilibrium constants depends primarily on the numbers and charges of ionic species in the reactions. Increasing ionic strength favors the side of the reaction with the larger sum of squared ion charges,  $\Delta z^2$ :

$$\Delta z^2 = \sum_i s_{i,p} z_{i,p}^2 - \sum_i s_{i,r} z_{i,r}^2, \quad (\text{A-4})$$

$$\sum_i s_{i,r} (\text{species})_{i,r} \rightarrow \sum_i s_{i,p} (\text{species})_{i,p}. \quad (\text{A-5})$$

In equation A-4, the  $s_{i,p}$  and  $s_{i,r}$  are the stoichiometric coefficients of the products and reactants in the reaction, represented by equation A-5; and the  $z_{i,r}$  and  $z_{i,p}$  are the corresponding charges of the species. Some examples follow:

Reaction	$\Delta z^2$	Side favored
$\text{Zn}^{2+} + 4\text{CN}^{1-} \rightarrow \text{Zn}(\text{CN})_4^{2-}$	-4	Left
$\text{HgCl}_2 + \text{Cl}^{1-} \rightarrow \text{HgCl}_3^{1-}$	0	Either
$\text{HgCl}_3^{1-} + \text{Cl}^{1-} \rightarrow \text{HgCl}_4^{2-}$	+2	Right
$2\text{AgCN(s)} \rightarrow \text{Ag}^{1+} + \text{Ag}(\text{CN})_2^{1-}$	+2	Right
$\text{Fe}^{3+} + \text{SO}_4^{2-} \rightarrow \text{FeSO}_4^{1+}$	-12	Left

Ionic strength affects reaction rates through the charges of the species that react in the rate-limiting step of the reaction. If the reacting species in the rate-limiting step are all neutral or involve only one ionic species, the effect of ionic strength on the rate is relatively insignificant. If two ionic species react in the rate-limiting step, the rate constant increases with increasing ionic strength if the charges of the two reacting ions have the same sign, and decreases with increasing ionic strength if their charges have opposite signs. This effect of ionic strength on reaction rates is termed the "salt effect" in the older literature.



## APPENDIX B.—THERMODYNAMIC DATA FOR FREE CYANIDE AND DERIVED SPECIES

This appendix contains tables of standard enthalpies of formation  $\Delta_f H^\circ$  and standard Gibbs energies of formation  $\Delta_f G^\circ$  (table B-1), equilibrium data at different temperatures and ionic strengths (table B-2), and solids solubility data (table B-3) for free cyanide and derived species. Some of the  $\Delta_f G^\circ$  data were calculated or estimated from the solubility data in table B-3 or other data; the details for other data are given in the footnotes of table B-1. The major data sources are the NBS tables (1),<sup>1</sup> the JANAF tables (2), a CODATA report (3), and the compilations by Christensen and others (4) and Martell and Smith (5-7). Other references are cited in the tables in the column "Additional references": cyanide (8-16), C(II) species (17-22), C(III) derivatives (23-35), C(IV) derivatives (36-69), and fulminate and derivatives (70-73). The oxide species, namely formate, oxalate, and carbonate, are also included in tables B-1 and B-2. Except for placing fulminate and its derivatives at the ends of the tables, we have used the same arrangement as that used in chapter 2.

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<sup>1</sup>Italic numbers in parentheses refer to items in the list of references at the end of this appendix.



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Table B-1.-Thermodynamic formation data for free cyanide and derived and related species at 25° c

Species	$\Delta_f H^\circ$ , kJ·mol <sup>-1</sup>	$\Delta_f G^\circ$ , kJ·mol <sup>-1</sup>	Additional references
HCN (g)	+135.1	+124.9	
HCN (aq)	+107.1	+119.8	
CN <sup>-</sup> (aq)	+150.6	+172.4	
CO (g)	-110.5±.1	-137.2±0.1	
HCONH <sub>2</sub> (l)	-254.0	-168.9	18
HCONH <sub>2</sub> (g)	-189.0	-143.8	18
HCONH <sub>2</sub> (aq)	-247.7	-180.9	19
HCO <sub>2</sub> H (aq)	-425.4	-372.3	
HCO <sub>2</sub> <sup>-</sup> (aq)	-425.5	-350.9	
C <sub>2</sub> N <sub>2</sub> (g)	+309.0	+297.4	
C <sub>2</sub> N <sub>2</sub> (aq)	N	+301.4	
H <sub>2</sub> NCSCSNH <sub>2</sub> (s)	-20.8	<sup>1</sup> +94.5	24
H <sub>2</sub> NCSCSNH <sub>2</sub> (aq)	N	+108.8	25
H <sub>2</sub> NCOCNH <sub>2</sub> (s)	<sup>2</sup> -262.6	<sup>2</sup> -124.5	
H <sub>2</sub> NCOCNH <sub>2</sub> (aq)	N	N	
H <sub>2</sub> NCOCNH <sub>2</sub> (s)	-504.4	-340.0	25, 28
H <sub>2</sub> NCOCNH <sub>2</sub> (aq)	N	-328.6	29
H <sub>2</sub> NCOCOOH (s)	-661.2	<sup>3</sup> -515.6	25, 31
H <sub>2</sub> NCOCOOH (aq)	N	<sup>4</sup> -506.6	32
H <sub>2</sub> NCOCO <sub>2</sub> <sup>-</sup> (aq)	N	-494.3	33
H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> (aq)	-815.1	-705.7	34-35
HC <sub>2</sub> O <sub>4</sub> (aq)	-818.4	-698.3	
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> (aq)	-825.1	-673.9	
ClCN (g)	-137.9	-131.0	
BrCN (g)	-186.2	-165.3	
NCNH <sub>2</sub> (s)	+59.0	<sup>5</sup> +128.9	
NCNH <sub>2</sub> (g)	+134.2	<sup>6</sup> +157.5	36
NCNH <sub>2</sub> (aq)	+74.5	<sup>7</sup> +126.1	37-38
NCNH <sup>-</sup> (aq)	N	+184.9	37, 40
HNCS (aq)	N	+98.4	41
NCS <sup>-</sup> (aq)	+76.4	+92.7	
NCSe <sup>-</sup> (aq)	+80.	+142.	42-43
CS <sub>2</sub> (l)	+89.2	+65.0	
CS <sub>2</sub> (g)	+116.9	+66.8	
CS <sub>2</sub> (aq)	+88.6	+74.3	44
HNCO (aq) <sup>8</sup>	-156.4	-117.4	45-46
NCO <sup>-</sup> (aq) <sup>8</sup>	-146.0	-97.4	
COS (g)	-138.4	-165.6	
COS (aq)		-156.0	47
CO <sub>2</sub> (g)	-393.5±0.1	-394.4±0.1	48
CO <sub>2</sub> (aq)	-413.3±0.2	-386.0±0.2	48
C(NH <sub>2</sub> ) <sub>3</sub> <sup>+</sup> (aq)	-139.1	<sup>9</sup> -12.	51-54



Table B-1.-Thermodynamic formation data for free cyanide and derived and related species at 25° C-Continued

Species	$\Delta_f H^\circ$ , kJ·mol <sup>-1</sup>	$\Delta_f G^\circ$ , kJ·mol <sup>-1</sup>	Additional references
HNC(NH <sub>2</sub> ) <sub>2</sub> (s)	-56.1	N	
HNC(NH <sub>2</sub> ) <sub>2</sub> (aq)	-63.1	+68.	56-58
CS(NH <sub>2</sub> ) <sub>2</sub> (s)	-89.1	<sup>10</sup> +19.8	36, 59-60
CS(NH <sub>2</sub> ) <sub>2</sub> (aq)	-66.5	<sup>11</sup> +18.3	61-63
CO(NH <sub>2</sub> ) <sub>2</sub> (s)	-333.5	-197.3	
CO(NH <sub>2</sub> ) <sub>2</sub> (aq)	-318.4	-203.3	61-63, 65
H <sub>2</sub> NCOOH (aq)	N	-418.6	66-67
H <sub>2</sub> NCO <sub>2</sub> <sup>-</sup> (aq)	-498.0	-378.1	66-67
HCO <sub>3</sub> <sup>-</sup> (aq)	-689.9±0.2	-586.9±0.2	48
C <sub>3</sub> <sup>2-</sup> (aq)	-675.2±0.2	-528.0±0.2	48
HCNO (aq) <sup>12</sup>	N	+152.	70-72
CNO <sup>-</sup> (aq) <sup>12</sup>	N	<sup>13</sup> +181.	70-71

N No data.

<sup>1</sup>Derived from estimated  $S^\circ$  of 141.3 J·K<sup>-1</sup> obtained by assuming  $\Delta_f S^\circ$  based on  $S_2(g)$  (reference 3) equal to  $\Delta_f S^\circ$  for H<sub>2</sub>NCOCONH<sub>2</sub>.

<sup>2</sup> $\Delta_f H^\circ$  taken as average of values for H<sub>2</sub>NCSCSNH<sub>2</sub> and H<sub>2</sub>NCOCONH<sub>2</sub>,  $\Delta_f G^\circ$  derived from estimated  $S^\circ$  of 135.5 J·K<sup>-1</sup>, which is the average of the published value for H<sub>2</sub>NCOCONH<sub>2</sub> (reference 28) and the estimated value for H<sub>2</sub>NCSCSNH<sub>2</sub>, increased by  $R \ln 2$ .

<sup>3</sup>Derived from estimated  $S^\circ$  of 122.6 J·K<sup>-1</sup>, which is the average of the published values for H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and H<sub>2</sub>NCOCONH<sub>2</sub> (references 31 and 28, respectively), increased by  $R \ln 2$ .

<sup>4</sup>Derived from solubility with correction for dissociation.

<sup>5</sup>Derived from vapor pressure and  $S^\circ$  of gas.

<sup>6</sup>Derived from  $S^\circ$  250 J·K<sup>-1</sup>, estimated from comparison of  $S^\circ$  values of XCH<sub>3</sub>(g) and XCN(g) (X = F, OH, NH<sub>2</sub>, CH<sub>3</sub>) tabulated in reference 1.

<sup>7</sup>Derived from infinite-dilution Raoultian activity coefficient of 18 estimated from data in reference 38.

<sup>8</sup>Cyanic acid, cyanate.

<sup>9</sup>Derived from published solubility and activity data and estimated  $S^\circ$  of 235 J·K<sup>-1</sup> for CN<sub>3</sub>H<sub>6</sub>ClO<sub>4</sub>; the latter was derived from estimated  $S^\circ$  of 215 J·K<sup>-1</sup> for CN<sub>3</sub>H<sub>6</sub>NO<sub>3</sub> and comparison of  $S^\circ$  values of nitrates and perchlorates of K, Rb, and NH<sub>4</sub> tabulated in reference 1. The estimated  $S^\circ$  for CN<sub>3</sub>H<sub>6</sub>NO<sub>3</sub> was assumed equal to the estimated  $S^\circ$  of CO(NH<sub>2</sub>)<sub>2</sub>HNO<sub>3</sub>, which was taken as equal to the sum of the  $S^\circ$  values for CO(NH<sub>2</sub>)<sub>2</sub> and HNO<sub>3</sub> (reference 1), with subtraction of 45.2 J·K<sup>-1</sup>, the entropy of melting of HNO<sub>3</sub> (reference 53).

<sup>10</sup>Derived from published vapor pressure and  $S^\circ$  of gas (references 36 and 60).

<sup>11</sup>Derived using estimated activity coefficient of 0.86 at saturation, taken as equal to that of CO(NH<sub>2</sub>)<sub>2</sub> at the same molality (reference 63).

<sup>12</sup>Fulminic acid, fulminate.

<sup>13</sup>Derived from log K for formation of aqueous Hg(CNO)<sub>2</sub> in reference 70 and solubility of Hg(CNO)<sub>2</sub> in reference 71. This required an estimated value of +342 kJ·mol<sup>-1</sup> for the standard Gibbs energy of formation of solid Hg(CNO)<sub>2</sub>, which was estimated from data in reference 1 for cyanates and fulminates of Hg, Ag, and Na.



Table B-2.-Equilibrium data for reactions of free cyanide and derived species

Reactant	Reaction type <sup>1</sup>	Temperature, °C	Log K at ionic strength (M)				Additional references
			0.0	0.1	1.0	3.0	
HCN	s	0	1.33	N	N	N	8-10
		10	1.16	N	N	N	
		25	.90	N	N	N	
		40	.68	N	N	N	
		60	.42	N	N	N	
		90	.12	N	N	N	
HCN	a	0	<sup>2</sup> 10.00	N	N	N	11-16
		10	9.63	N	N	N	
		25	9.21	9.05	8.88	8.81	
		<sup>3</sup> 25	9.21	9.04	8.95	9.22	
		40	8.88	N	N	N	
		60	8.4	N	N	N	
		90	8.0	N	N	N	
CO	s	0	-2.81	N	N	N	9
		10	-2.91	N	N	N	
		25	-3.03	N	N	N	
		40	-3.11	N	N	N	
		60	-3.17	N	N	N	
H-CS-SH	a	25	.85	N	N	N	17
H-CO-NH <sub>3</sub> <sup>+</sup>	a	25	-.2	N	<sup>4</sup> .1	N	20-21
H-CO-NH <sub>2</sub>	a	25	N	N	13.	N	22
H-CO-SH	a	25	2.06	N	N	N	17
HCO-OH	a	0	3.79	N	N	N	
		10	3.76	N	N	N	
		25	3.75	3.57	3.49	3.90	
		40	3.77	N	N	N	
		60	3.81	N	N	N	
NC-CN	s	25	-.7	N	N	N	8
NC-CO-NH <sub>2</sub>	a	25	N	<sup>5</sup> 10.8	N	N	23
H <sub>2</sub> N-CS-CS-NH <sub>2</sub>	a	25	11.0	10.8	10.8	N	26
H <sub>2</sub> N-CS-CS-NH <sup>-</sup>	a	25	N	N	13.1	N	
H <sub>2</sub> N-CO-CS-NH <sub>2</sub>	a	25	11.5	11.3	11.2	N	27
HS-CO-CO-SH	a	25	.9	N	N	N	30
HS-CO-COS <sup>-</sup>	a	25	2.7	N	N	N	30



Table B-2.-Equilibrium data for reactions of free cyanide and derived species-Continued

Reactant	Reaction type <sup>1</sup>	Temperature, °C	Log K at ionic strength (M)				Additional references
			0.0	0.1	1.0	3.0	
H <sub>2</sub> N-CO-CO-OH	a	25	2.75	N	N	N	33
H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	a	<sup>3</sup> 0	1.25	1.01	.80	.88	34-35
		<sup>3</sup> 10	1.25	1.01	.80	.90	
		25	1.28	1.04	1.04	1.26	
		<sup>3</sup> 25	1.28	1.03	.82	.93	
		<sup>3</sup> 40	1.32	1.07	.86	.96	
		<sup>3</sup> 60	1.42	1.14	.92	.99	
		<sup>3</sup> 90	1.53	1.25	1.02	1.06	
HC <sub>2</sub> O <sub>4</sub> <sup>-</sup>	a	<sup>3</sup> 0	4.22	3.80	3.51	3.61	35
		<sup>3</sup> 10	4.24	3.81	3.50	3.58	
		25	4.28	3.83	3.56	3.81	
		<sup>3</sup> 25	4.28	3.83	3.50	3.55	
		<sup>3</sup> 40	4.36	3.89	3.53	3.54	
		<sup>3</sup> 60	4.48	3.99	3.60	3.55	
		<sup>3</sup> 90	4.71	4.18	3.74	3.62	
NC-NH <sub>3</sub> <sup>+</sup>	a	25	N	1.1	<sup>6</sup> -1.1	N	39
NC-NH <sub>2</sub>	a	25	10.3	N	<sup>6</sup> 10.7	N	37, 40
NC-NH <sup>1-</sup>	a	25	11.6	N	N	N	37
HNCS	a	25	1.6	N	N	N	41
HNCO	a	0	3.77	N	N	N	45-46
		10	3.62	3.7	N	N	
		25	3.47	N	N	N	
		40	3.43	N	N	N	
CO <sub>2</sub>	s	<sup>3</sup> 0	-1.11	-1.12	-1.23	-1.43	48-51
		<sup>3</sup> 10	-1.27	-1.28	-1.38	-1.56	
		<sup>3</sup> 25	-1.47	-1.48	-1.56	-1.73	
		25	-1.47	-1.52	-1.53	-1.56	
		<sup>3</sup> 40	-1.62	-1.63	-1.71	-1.87	
		<sup>3</sup> 60	-1.78	-1.79	-1.87	-2.04	
		<sup>3</sup> 90	-1.94	-1.95	-2.04	-2.20	
C(NH <sub>2</sub> ) <sub>3</sub> <sup>+</sup>	a	25	<sup>7</sup> 14.	N	13.5	N	56-57
H <sub>2</sub> N-CS-SH	a	25	2.95	N	N	N	64
H <sub>2</sub> N-CO-OH	a	25	<sup>8</sup> 7.1	N	<sup>4</sup> 6.8	N	66-67
		40	N	N	<sup>4</sup> 6.6	N	
		60	N	N	<sup>4</sup> 6.5	N	
H <sub>2</sub> CO <sub>3</sub>	a	<sup>3</sup> 0	6.57	6.35	6.17	6.16	48, 51, 68
		<sup>3</sup> 10	6.45	6.23	6.05	6.05	
		<sup>3</sup> 25	6.35	6.12	5.94	5.96	



Table B-2.-Equilibrium data for reactions of free cyanide and derived species-Continued

Reactant	Reaction type <sup>1</sup>	Temperature, °C	Log K at ionic strength (M)				Additional references
			0.0	0.1	1.0	3.0	
HCO <sub>3</sub> <sup>-</sup>	a	25	6.35	6.14	5.99	6.44	48, 51, 69
		<sup>3</sup> 40	6.30	6.06	5.88	5.90	
		<sup>3</sup> 60	6.28	6.03	5.84	5.86	
		<sup>3</sup> 90	6.35	6.08	5.86	5.85	
		<sup>3</sup> 0	10.63	10.18	9.83	9.87	
		<sup>3</sup> 10	10.49	10.04	9.65	9.67	
		<sup>3</sup> 25	10.33	9.87	9.48	9.47	
		<sup>3</sup> 25	10.33	9.93	9.57	9.63	
		<sup>3</sup> 40	10.23	9.75	9.33	9.31	
		<sup>3</sup> 60	10.14	9.64	9.19	9.13	
HCNO	a	<sup>3</sup> 90	10.11	9.56	9.05	8.93	72
		25	5.	N	N	N	
H-CO-NH-OH	a	25	8.78	N	N	N	73
		40	<sup>9</sup> 8.62	N	N	N	

N No data.

<sup>1</sup>a, acid dissociation, pK<sub>a</sub> tabulated; b, base dissociation, pK<sub>b</sub> tabulated; s, solubility, log (molal solubility) tabulated.<sup>2</sup>Extrapolated.<sup>3</sup>NaCl solutions.<sup>4</sup>Ionic strength 0.5M.<sup>5</sup>Ionic strength 0.2M.<sup>6</sup>Ionic strength 2.0M.<sup>7</sup>Estimated.<sup>8</sup>Estimated by adding log K values for the reactions NH<sub>3</sub> + HCO<sub>3</sub><sup>-</sup> = H<sub>2</sub>NCO<sub>2</sub><sup>-</sup> + H<sub>2</sub>O, H<sub>2</sub>NCO<sub>2</sub>H + H<sub>2</sub>O = NH<sub>3</sub> + CO<sub>2</sub> + H<sub>2</sub>O, and CO<sub>2</sub> + H<sub>2</sub>O = HCO<sub>3</sub><sup>-</sup> + H<sup>+</sup>, assuming zero ionic-strength dependence of log K for the first two of these reactions.<sup>9</sup>Extrapolated from data at 25° and 35° C assuming linear relationship of log K to reciprocal absolute temperature.



Table B-3.-Solubilities of solid compounds derived  
from cyanide in water at 25° C

Compound	Solubility, mol·kg water	References
$\text{H}_2\text{N-CS-CS-NH}_2$	0.0031	25
$\text{H}_2\text{N-CS-CO-NH}_2$	N	
$\text{H}_2\text{N-CO-CO-NH}_2$	.01	29
$\text{H}_2\text{N-CO-CO-OH}$	.04	32
$\text{NC-NH}_2$	N	
$\text{CO}(\text{NH}_2)_2$	20.2	62, 65
$\text{CS}(\text{NH}_2)_2$	2.17	62

N No data.



## APPENDIX C.—THERMODYNAMIC DATA FOR AUXILIARY SPECIES

This appendix contains tables of standard enthalpies of formation  $\Delta_f H^\circ$  and standard Gibbs energies of formation  $\Delta_f G^\circ$  (table C-1) and equilibrium data at different temperatures and ionic strengths (table C-2) for auxiliary species. The major data sources are the NBS tables (1), a CODATA report (2), the compilations by Christensen and others, (3) and Martell and Smith (4-6). A review by Wilhelm and others (7) provided references for gas solubilities. Primary-source references for additional data are listed in the column "Additional references": species containing only oxygen or hydrogen (8-11), chlorine and bromine species (12-19), sulfur species (20-37), selenium species (38-41), nitrogen species (24, 42-48), and arsenic species (49). Carbon species data are compiled in appendix B.

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<sup>1</sup>Italic numbers in parentheses refer to items in the list of references at the end of this appendix.



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Table C-1.-Thermodynamic formation data for auxiliary species at 25° C

Species	$\Delta_f H^\circ$ , kJ·mol <sup>-1</sup>	$\Delta_f G^\circ$ , kJ·mol <sup>-1</sup>	Additional references
O <sub>2</sub> (aq)	-11.7	+16.5	
O <sub>3</sub> (g)	+143.	+163.	
O <sub>3</sub> (aq)	+126.	+174.	9
H <sub>2</sub> O (l)	-285.8±0.1	-237.2±0.1	
H <sup>+</sup> (aq)	0.0	0.0	
OH <sup>-</sup> (aq)	-230.0±0.1	-157.3±0.1	
H <sub>2</sub> O <sub>2</sub> (aq)	-191.2	-134.0	
HO <sub>2</sub> <sup>-</sup> (aq)	-159.4	-67.4	11
Cl <sup>-</sup> (aq)	-167.1±0.1	-131.2±0.1	
Cl <sub>2</sub> (aq)	-23.4	+6.9	
HClO (aq)	-120.9	-79.8	12-13
ClO <sup>-</sup> (aq)	-107.1	-36.8	
HClO <sub>2</sub> (aq)		+38	14-16
ClO <sub>2</sub> <sup>-</sup> (aq)		+27	14
ClO <sub>2</sub> (g)	+102. ±3	+120. ±3	17
ClO <sub>2</sub> (aq)		+117.	15
ClO <sub>3</sub> <sup>-</sup> (aq)	-104.1	-7.9	18
Br <sup>-</sup> (aq)	-121.5±0.1	-104.0±0.1	
Br <sub>2</sub> (g)	+30.9	+3.1	
Br <sub>2</sub> (aq)	-2.6	+3.9	
HBrO (aq)	-113.0	-82.7	19
BrO <sup>-</sup> (aq)	-94.1	-33.4	
BrO <sub>3</sub> <sup>-</sup> (aq)	-66.7	+19.1	18



Table C-1.--Thermodynamic formation data for auxiliary species at 25° C--Continued

Species	$\Delta_f H^\circ$ , $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_f G^\circ$ , $\text{kJ}\cdot\text{mol}^{-1}$	Additional references
$\text{HSeO}_4^-$ (aq)	-576.1	-450.8	40-41
$\text{SeO}_4^{2-}$ (aq)	-599.1	-441.3	
$\text{NH}_3$ (g)	-45.9 $\pm$ 0.4	-16.4 $\pm$ 0.4	
$\text{NH}_3$ (aq)	-81.4 $\pm$ 0.3	-26.5 $\pm$ 0.3	
$\text{NH}_4^+$ (aq)	-133.3 $\pm$ 0.3	-79.3 $\pm$ 0.3	
$\text{HNO}_2$ (aq)	-119.2	-50.9	47-48
$\text{NO}_2^-$ (aq)	-104.6	-32.2	
$\text{NO}_3^-$ (aq)	-206.9 $\pm$ 0.4	-110.9 $\pm$ 0.4	
$\text{AsH}_3$ (g)	+62.8	+65.3	49
$\text{AsH}_3$ (aq)	N	+77.0	
$\text{As}(\text{OH})_3$ (aq)	-742.2	-639.8	
$\text{AsO}(\text{OH})_2^-$ (aq)	-714.7	-587.1	
$\text{H}_3\text{AsO}_4$ (aq)	-902.5	-766.0	
$\text{H}_2\text{AsO}_4^-$ (aq)	-909.6	-753.2	
$\text{HAsO}_4^{2-}$ (aq)	-906.3	-714.6	
$\text{AsO}_4^{3-}$ (aq)	-888.1	-648.8	

N No data.



Table C-2.-Equilibrium data for reactions of auxiliary species

Reactant	Reaction type <sup>1</sup>	Temperature, °C	Log K at ionic strength (M)				Additional references
			0.0	0.1	1.0	3.0	
O <sub>2</sub>	s	<sup>2</sup> 0	-2.67	N	N	N	8
		<sup>2</sup> 10	-2.77	-2.78	-2.92	N	
		<sup>2</sup> 25	-2.90	-2.91	-3.04	N	
		<sup>2</sup> 40	-2.98	-2.99	-3.10	N	
		<sup>2</sup> 60	-3.05	-3.06	-3.13	N	
O <sub>3</sub>	s	<sup>3</sup> 0	<sup>4</sup> -1.63	<sup>4</sup> -1.63	<sup>4</sup> -1.69	N	9
		<sup>3</sup> 10	-1.78	-1.79	-1.88	N	
		<sup>3</sup> 25	-1.95	-1.96	-2.10	N	
		<sup>3</sup> 40	<sup>4</sup> -2.10	<sup>4</sup> -2.12	<sup>4</sup> -2.30	N	
H <sub>2</sub> O	a	<sup>2</sup> 0	14.94	14.74	14.68	14.93	10
		<sup>2</sup> 10	14.53	14.32	14.26	14.51	
		25	14.00	13.78	13.79	14.18	
		<sup>2</sup> 25	14.00	13.78	13.72	13.97	
		<sup>2</sup> 40	13.54	13.32	13.26	13.50	
		<sup>2</sup> 60	13.02	12.79	12.70	12.92	
		<sup>2</sup> 90	12.42	12.17	12.05	12.24	
H <sub>2</sub> O <sub>2</sub>	a	10	11.98	N	N	N	11
		25	11.67	N	11.39	N	
		40	11.39	N	N	N	
Cl <sub>2</sub>	s	25	-1.21	N	N	N	
HClO	a	0	7.82	N	N	N	12-13
		10	7.70	N	N	N	
		25	7.53	N	N	N	
		40	7.45	N	N	N	
		60	<sup>4</sup> 7.40	N	N	N	
HClO <sub>2</sub>	a	25	2.0	1.88	1.72	N	15-16
HBrO	a	0	<sup>4</sup> 9.32	N	N	N	19
		10	<sup>4</sup> 8.97	N	N	N	
		25	8.63	N	N	N	
		40	8.44	N	N	N	
		60	<sup>4</sup> 8.28	N	N	N	
H <sub>2</sub> S	s	0	-.67	N	N	N	20-23
		10	-.81	N	N	N	
		25	-.99	-1.00	-1.05	-1.17	
		40	-1.17	N	N	N	
		60	-1.37	N	N	N	
		90	-1.89	N	N	N	
H <sub>2</sub> S	a	0	7.43	N	N	N	24-26
		10	7.23	N	N	N	
		25	7.02	6.82	6.66	6.87	
		40	6.81	N	N	N	
		60	6.64	N	N	N	
		90	6.51	N	N	N	



Table C-2.-Equilibrium data for reactions of auxiliary species—Continued

Reactant	Reaction type <sup>1</sup>	Temperature, °C	Log K at ionic strength (M)				Additional references
			0.0	0.1	1.0	3.0	
SH <sup>-</sup>	a	25	17.	N	N	N	27
HS <sub>2</sub> O <sub>3</sub> <sup>-</sup>	a	25	1.6	N	N	N	
SO <sub>2</sub>	s	25	.09	N	.03	.06	31
H <sub>2</sub> SO <sub>3</sub>	a	25	1.87	1.62	1.37	1.72	31
HSO <sub>3</sub> <sup>-</sup>	a	25	7.17	N	6.34	6.36	31-32
		40	7.41	N	N	N	
		60	7.49	N	N	N	
		90	7.55	N	N	N	
HSO <sub>4</sub> <sup>-</sup>	a	<sup>2</sup> 0	1.78	1.20	.79	.74	33-34
		<sup>2</sup> 10	1.85	1.31	.89	.82	
		25	1.99	1.55	1.10	.91	
		<sup>2</sup> 25	1.99	1.49	1.06	.97	
		<sup>2</sup> 40	2.15	1.68	1.24	1.13	
		<sup>2</sup> 60	2.40	1.96	1.49	1.35	
		<sup>2</sup> 90	2.82	2.37	1.85	1.67	
HSO <sub>5</sub>	a	25	10.1	N	N	N	35
H <sub>2</sub> Se	s	0	<sup>4</sup> -.84	N	N	N	38
		10	<sup>4</sup> -.94	N	N	N	
		25	-1.08	N	N	N	
		40	-1.21	N	N	N	
		60	<sup>4</sup> -1.35	N	N	N	
		90	<sup>4</sup> -1.54	N	N	N	
H <sub>2</sub> Se	a	25	3.9	N	3.5	N	
SeH <sup>-</sup>	a	25	15.	N	N	N	
H <sub>2</sub> SeO <sub>3</sub>	a	25	2.62	N	2.27	2.61	39
HSeO <sub>3</sub> <sup>-</sup>	a	25	8.25	N	7.78	8.05	92
HSeO <sub>4</sub> <sup>-</sup>	a	0	1.36	N	N	N	40-41
		10	1.46	N	N	N	
		25	1.66	N	N	N	
		40	1.89	N	N	N	
		60	<sup>3</sup> 2.25	N	N	N	
		90	<sup>4</sup> 2.92	N	N	N	



Table C-2.-Equilibrium data for reactions of auxiliary species—Continued

Reactant	Reaction type <sup>1</sup>	Temperature, °C	Log K at ionic strength (M)				Additional references
			0.0	0.1	1.0	3.0	
NH <sub>3</sub>	s	0	2.33	N	N	N	42-44
		10	2.10	N	N	N	
		25	1.78	N	1.60	N	
		40	1.47	N	1.31	N	
		60	1.11	N	.97	N	
		90	.66	N	N	N	
NH <sub>3</sub>	b	<sup>5</sup> 0	4.86	4.65	4.46	4.40	24, 45-46
		<sup>5</sup> 10	4.80	4.58	4.40	4.35	
		<sup>5</sup> 25	4.75	4.53	4.34	4.29	
		<sup>5</sup> 40	4.73	4.50	4.30	4.26	
		<sup>5</sup> 60	4.74	4.50	4.29	4.24	
		<sup>5</sup> 90	4.82	4.56	4.33	4.27	
HNO <sub>2</sub>	a	25	3.28	N	N	N	47-48
AsH <sub>3</sub>	s	10	-1.88	N	N	N	
		25	-2.05	N	N	N	
As(OH) <sub>3</sub>	a	25	9.23	N	9.07	N	
H <sub>3</sub> AsO <sub>4</sub> <sup>-</sup>	a	25	2.25	N	N	N	
H <sub>2</sub> AsO <sub>4</sub>	a	25	6.77	N	N	N	
HAsO <sub>4</sub> <sup>2-</sup>	a	25	11.53	N	N	N	

N No data.

<sup>1</sup>a, acid dissociation, pK<sub>a</sub> tabulated; b, base dissociation, pK<sub>b</sub> tabulated; s, solubility, log (molal solubility) tabulated.<sup>2</sup>NaCl solutions.<sup>3</sup>Na<sub>2</sub>SO<sub>4</sub> solutions.<sup>4</sup>Extrapolated.<sup>5</sup>KCl solutions.



## APPENDIX D.—THERMODYNAMIC DATA FOR METAL SPECIES

This appendix contains tables of standard Gibbs free energies of formation  $\Delta_f G^\circ$  and equilibrium data at 25° C and different ionic strengths for aqueous metal ions (table D-1) and other metal species (tables D-2 through D-23). The major data sources are the NBS tables (1),<sup>1</sup> a CODATA report (2), the compilations by Martell and Smith (3-5), Baes and Mesmer (6), the U.S. Bureau of Mines (7, 8), Mills (9), Sharpe (10), and Beck (11). Primary-source references are cited in the tables in the column "Additional references": Zn (12-17), Cd (12, 18-20), Hg (19, 21-24), Cu (25-29), Ag (30), Au (30-39), Ni (27, 40, 41), Co (27, 42-56), Fe (27, 57-68), Mn (43, 69-75), Cr (50, 53, 76-79), Tl (80, 81), and Pb (82-85).

Because Tl(III) forms strong cyanide complexes, the question arises as to whether Ga(III) and In(III) also form cyanide complexes. No equilibrium data exist for aqueous gallium or indium cyanide species. An analysis of equilibrium data for the oxide solid phases and aqueous hydroxide species of Cu(I), Ag(I), Au(I), Zn(II), Cd(II), Hg(II), Ga(III), In(III), and Tl(III), and the known cyanide species of these metals, was conducted to generate estimates of log K values for Ga(III) and In(III) cyanide species. The data for Ga(III) and In(III) are compiled in table D-24. The values obtained are relatively low, and consequently Ga(III) and In(III) cyanide species are not expected to be important.

Heavy-metal selenide minerals can be leached by cyanide solutions, probably with formation of dissolved selenium cyanide ( $\text{SeCN}^-$ ). The standard Gibbs free energies of formation of some heavy-metal selenides are listed in table D-25. Some of the data are from compilations (1, 9, 86), other data are from elsewhere (87-92).

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<sup>1</sup>Italic numbers in parentheses refer to items in the list of references at the end of this appendix.



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Table D-1.-Standard Gibbs free energies of formation  
of aqueous metal ions at 25° C

Ion	$\Delta_f G^\circ$ , kJ·mol <sup>-1</sup>	References
Zn <sup>2+</sup>	-147.0± 0.2	12
Cd <sup>2+</sup>	-77.6± 0.2	12
Hg <sup>2+</sup>	153.6± 0.2	21
Hg <sub>2</sub> <sup>2+</sup>	164.6± 0.2	21
Cu	48.9± 0.2	25, 26
Cu <sup>2+</sup>	65.2± 0.4	25, 27
Ag	77.1± 0.1	
Au	164.± 3.	31, 32
Au <sup>3+</sup>	<sup>1</sup> 434.2±30.	31
Ni <sup>2+</sup>	-44.4± 0.4	27
Co <sup>2+</sup>	-55.8± 0.4	27
Co <sup>3+</sup>	<sup>2</sup> 125.6± 1.1	42
Fe <sup>2+</sup>	-91.3± 0.6	27, 57, 58
Fe <sup>3+</sup>	<sup>3</sup> -17.0± 0.8	57, 58
Mn <sup>2+</sup>	-231. ± 2.	68
Mn <sup>3+</sup>	<sup>4</sup> -81.4± 2.5	69
Cr <sup>3+</sup>	-226. ±10.	75
Tl	-31.6±0.1	79
Tl <sup>3+</sup>	+215.	
Pb <sup>2+</sup>	-24.0	
Mg <sup>2+</sup>	-456.0	
Ca <sup>2+</sup>	-553.1	

<sup>1</sup>Derived from the value for Au and value of +1,5±0.1 V for standard reduction potential for Au<sup>3+</sup> + 2e<sup>-</sup> = Au.

<sup>2</sup>Derived from value for Co<sup>2+</sup> and value of +1,88±0.01 V for standard reduction potential for Co<sup>3+</sup> + e<sup>-</sup> = Co<sup>2+</sup>.

<sup>3</sup>Derived from value for Fe<sup>2+</sup> and value of +0.77±0.01 V for standard reduction potential for Fe<sup>3+</sup> + e<sup>-</sup> = Fe<sup>2+</sup>.

<sup>4</sup>Derived from value for Mn<sup>2+</sup> and value of +1.55±0.01 V for standard reduction potential for Mn<sup>3+</sup> + e<sup>-</sup> = Mn<sup>2+</sup>.



Table D-2.--Thermodynamic data for zinc(II) species at 25° C

Reaction	Log K at ionic strength (M)				-Δ <sub>f</sub> G° of underlined species kJ·mol <sup>-1</sup>	Additional references
	0.0	0.1	1.0	3.0		
$\text{Zn}^{2+} + n\text{OH}^- = \underline{\text{Zn}(\text{OH})_n}^{2-n}, n = 1$	5.0	N	N	3.8	332.8	
2	10.2	N	N	8.3	519.8	
3	13.9	N	N	13.7	698.2	
4	15.5	N	N	18.0	864.7	
$2\text{Zn}^{2+} + \text{OH}^- = \underline{\text{Zn}_2(\text{OH})}^{3+}$	5.0	N	N	5.5	479.8	
$\underline{\text{ZnO}}(\text{s}) + \text{H}_2\text{O} = \text{Zn}^{2+} + 2\text{OH}^-$	-16.7	N	N	N	320.	
$\underline{\text{Zn}(\text{OH})_2}(\text{cr}) = \text{Zn}^{2+} + 2\text{OH}^-$	-16.5	N	N	N	555.8	
$\underline{\text{Zn}(\text{OH})_2}(\text{am}) = \text{Zn}^{2+} + 2\text{OH}^-$	-15.5	N	N	N	550.1	
$\text{Zn}^{2+} + n\text{Cl}^- = \underline{\text{ZnCl}}_n^{2-n}, n = 1$	.5	N	0.0	-.2	281.1	
2	.6	N	.0	-.4	412.8	
3	.5	N	-.1	0.0	543.5	
4	.2	N	N	-.7	672.9	
$\underline{\text{ZnS}}(\text{s}) + 2\text{H}^+ = \text{Zn}^{2+} + \text{H}_2\text{S}$	-4.4	N	N	N	200.	
$\text{Zn}^{2+} + n\text{SH}^- = \underline{\text{Zn}(\text{SH})_n}^{2-n}, n = 1$	<sup>1</sup> 7.	N	N	N	174.7	13
2	<sup>1</sup> 13.	N	N	N	196.6	13
3	<sup>1</sup> 14.	N	N	N	190.0	13
4	<sup>1</sup> 14.	N	N	N	177.7	13
$\text{Zn}^{2+} + n\text{S}_2\text{O}_3^{2-} = \underline{\text{Zn}(\text{S}_2\text{O}_3)_n}^{2-2n}, n = 1$	2.4	N	N	1.0	683.2	
2	<sup>2</sup> 4.7	N	N	1.9	1,218.8	
3	<sup>2</sup> 4.9	N	N	3.3	1,742.5	
$2\text{Zn}^{2+} + 2\text{S}_2\text{O}_3^{2-} = \underline{\text{Zn}_2(\text{S}_2\text{O}_3)_2}$	<sup>3</sup> 8.6	N	N	5.8	1,388.1	
$\text{Zn}^{2+} + n\text{SO}_4^{2-} = \underline{\text{Zn}(\text{SO}_4)_n}^{2-2n}, n = 1$	2.3	N	.9	.7	904.6	
2	<sup>4</sup> 3.7	N	1.2	.7	1,657.1	



Table D-2.-Thermodynamic data for zinc(II) species at 25° C-Continued

Reaction	Log K at ionic strength (M)				$-\Delta_f G^\circ$ of underlined species $\text{kJ}\cdot\text{mol}^{-1}$	Additional references
	0.0	0.1	1.0	3.0		
$\text{Zn}^{2+} + n\text{NH}_3 = \underline{\text{Zn}(\text{NH}_3)_n^{2+}}$ , $n = 1$	2.2	N	2.3	N	186.1	
2	4.5	N	4.8	N	225.7	
3	6.9	N	7.1	N	265.9	
4	8.9	N	9.3	N	303.8	
$\text{Zn}^{2+} + \text{HCO}_3 = \underline{\text{Zn}(\text{HCO}_3)}$	0.7	N	N	0.3	737.9	
$\text{Zn}^{2+} + n\text{CO}_3^{2-} = \underline{\text{Zn}(\text{CO}_3)_n^{2-2n}}$ , $n = 1$	5.1	N	N	4.2	704.1	
$n = 2$	<sup>5</sup> 8.1	N	N	N	1,249.2	
$\underline{\text{ZnCO}_3(\text{s})} = \text{Zn}^{2+} + \text{CO}_3^{2-}$	-10.8	N	N	N	736.6	14
$\underline{\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2(\text{s})} = 5\text{Zn}^{2+} + 6\text{OH}^-$ $+ 2\text{CO}_3^{2-}$	-74.3	N	N	N	3,158.9	14
$\text{Zn}^{2+} + n\text{NCS}^- = \underline{\text{Zn}(\text{NCS})_n^{2-n}}$ , $n = 1$	1.3	1.1	0.7	<sup>6</sup> 0.9	61.7	
2	1.9	N	1.0	<sup>6</sup> 1.4	-27.6	
3	2.0	N	1.2	<sup>6</sup> 1.7	-119.7	
4	1.6	N	1.5	<sup>6</sup> 2.2	-214.7	
$\text{Zn}^{2+} + n\text{CN}^- = \underline{\text{Zn}(\text{CN})_n^{2-n}}$ , $n = 1$	5.4	N	N	5.3	5.4	
2	11.1	10.6	N	11.0	-134.4	15
3	16.0	15.7	N	16.7	-278.9	15
4	19.6	20.0	N	21.6	-430.7	15, 16
$\underline{\text{Zn}(\text{CN})_2(\text{s})} = \text{Zn}(\text{CN})_2$	-4.5	N	N	-4.5	-108.8	17

N No data.

<sup>1</sup>Extrapolated to 25° C.<sup>2</sup>Estimated from ionic-strength dependence for reactions of corresponding Cd complexes.<sup>3</sup>Estimated by assuming zero ionic-strength dependence for  $2\text{Zn}(\text{S}_2\text{O}_3) = \text{Zn}_2(\text{S}_2\text{O}_3)_2$ .<sup>4</sup>Estimated from ionic-strength dependence for corresponding reactions of other divalent metal ions.<sup>5</sup>Estimated from data for corresponding complexes of other divalent metal ions.<sup>6</sup>Interpolated.



Table D-3.-Thermodynamic data for cadmium(II) species at 25° c

Reaction	Log K at ionic strength (M)				-Δ <sub>f</sub> G° of underlined species kJ·mol <sup>-1</sup>	Additional references
	0.0	0.1	1.0	3.0		
$\text{Cd}^{2+} + n\text{OH}^- = \underline{\text{Cd}(\text{OH})_n}^{2-n}$ , n = 1	3.9	N	N	4.0	257.2	
2	7.7	N	N	7.7	436.2	
3	7.8	N	N	N	594.0	
4	8.0	N	N	N	752.5	
$2\text{Cd}^{2+} + \text{OH}^- = \underline{\text{Cd}_2(\text{OH})}^{3+}$	4.6	N	N	5.1	338.8	
$\underline{\text{CdO}}(\text{s}) + \text{H}_2\text{O} = \text{Cd}^{2+} + 2\text{OH}^-$	-13.1	N	N	N	228.	
$\underline{\text{Cd}(\text{OH})_2}(\text{cr}) = \text{Cd}^{2+} + 2\text{OH}^-$	-14.4	N	N	N	470.4	
$\underline{\text{Cd}(\text{OH})_2}(\text{am}) = \text{Cd}^{2+} + 2\text{OH}^-$	-13.7	N	N	N	470.4	
$\text{Cd}^{2+} + n\text{Cl}^- = \underline{\text{CdCl}_n}^{2-n}$ , n = 1	2.0	1.5	1.4	1.5	220.2	
2	2.6	N	1.7	2.2	354.8	
3	2.4	N	1.5	2.3	484.9	
4	1.7	N	N	1.6	612.1	
$\underline{\text{CdS}}(\text{s}) + 2\text{H}^+ = \text{Cd}^{2+} + \text{H}_2\text{S}$	-7.1	N	N	N	146.	
$\text{Cd}^{2+} + n\text{SH}^- = \underline{\text{Cd}(\text{SH})_n}^{2-n}$ , n = 1	<sup>1</sup> 8.1	N	7.6	N	111.5	
2	<sup>1</sup> 15.1	N	14.6	N	139.2	
3	<sup>1</sup> 17.0	N	16.5	N	137.7	
4	<sup>1</sup> 19.4	N	18.9	N	139.1	
$\text{Cd}^{2+} + n\text{S}_2\text{O}_3^{2-} = \underline{\text{Cd}(\text{S}_2\text{O}_3)_n}^{2-2n}$ , n = 1	3.9	3.2	2.8	2.7	622.4	
2	6.3	N	4.6	4.7	1,158.6	
3	<sup>2</sup> 7.3	N	6.4	6.9	1,686.8	
$2\text{Cd}^{2+} + 2\text{S}_2\text{O}_3^{2-} = \underline{\text{Cd}_2(\text{S}_2\text{O}_3)_2}$	<sup>3</sup> 13.6	N	N	11.2	1,277.8	
$\text{Cd}^{2+} + n\text{SO}_4^{2-} = \underline{\text{Cd}(\text{SO}_4)_n}^{2-2n}$ , n = 1	2.5	N	1.0	.7	836.4	
2	<sup>4</sup> 3.8	N	1.6	.9	1,588.3	
$\text{Cd}^{2+} + n\text{NH}_3 = \underline{\text{Cd}(\text{NH}_3)_n}^{2+}$ , n = 1	2.5	N	2.6	N	118.4	
2	4.6	N	4.8	N	156.9	
3	5.9	N	6.2	N	190.8	
4	6.7	N	7.1	N	221.8	



Table D-3.-Thermodynamic data for cadmium(II) species at 25° C—Continued

Reaction	Log K at ionic strength ( <u>M</u> )				$-\Delta_f G^\circ$ of underlined species $\text{kJ}\cdot\text{mol}^{-1}$	Additional references
	0.0	0.1	1.0	3.0		
$\text{Cd}^{2+} + \text{HCO}_3^- = \underline{\text{Cd}(\text{HCO}_3)} \quad \text{_____}$	<sup>5</sup> 2.1	N	N	N	676.5	18
$\text{Cd}^{2+} + n\text{CO}_3^{2-} = \underline{\text{Cd}(\text{CO}_3)_n} \text{_____}, \quad \begin{matrix} n = 1 \\ n = 2 \end{matrix}$	<sup>5</sup> 3.5 <sup>5</sup> 6.4	N N	N N	N N	625.6 1,170.1	
$\underline{\text{CdCO}_3(\text{s})} = \text{Cd}^{2+} + \text{CO}_3^{2-}$	-12.0	N	N	-11.2	674.1	
$\text{Cd}^{2+} + n\text{NCS}^- = \underline{\text{Cd}(\text{NCS})_n} \text{_____}, \quad \begin{matrix} n = 1 \\ 2 \\ 3 \\ 4 \end{matrix}$	1.9 2.8 2.9 2.3	1.6 2.3 N N	1.3 2.0 2.1 1.9	1.4 2.2 2.5 2.5	-4.3 -91.8 -183.9 -280.1	
$\text{Cd}^{2+} + n\text{CN}^- = \underline{\text{Cd}(\text{CN})_n} \text{_____}, \quad \begin{matrix} n = 1 \\ 2 \\ 3 \\ 4 \end{matrix}$	6.0 11.1 15.6 17.9	N N N N	N N N N	5.6 10.8 15.7 19.2	-60.6 -203.8 -350.6 -509.8	19, 20
$\underline{\text{Cd}(\text{CN})_2(\text{s})} = \text{Cd}(\text{CN})_2$	<sup>6</sup> -1.3	N	N	N	-196.4	

N No data.

<sup>1</sup>Estimated from ionic-strength dependence for reactions of corresponding halide and NCS<sup>-</sup> complexes.

<sup>2</sup>Estimated from data for corresponding Hg complexes.

<sup>3</sup>Estimated by assuming zero ionic-strength dependence for  $2\text{Cd}(\text{S}_2\text{O}_3) = \text{Cd}_2(\text{S}_2\text{O}_3)_2$ .

<sup>4</sup>Estimated from ionic-strength dependence for corresponding reactions of other divalent metal ions.

<sup>5</sup> Estimated from data at ionic strength 0.05M and corresponding data for complexes of other divalent metal ions.

<sup>6</sup>Calculated from published solubility and complex formation data.



Table D-4.-Thermodynamic data for mercury(I) species at 25° C

Reaction	Log K at ionic strength (M)				$-\Delta_f G^\circ$ of underlined species $\text{kJ}\cdot\text{mol}^{-1}$	Additional references
	0.0	0.1	1.0	3.0		
$\text{Hg}_2^{2+} + \text{OH}^- = \underline{\text{Hg}_2(\text{OH})}$	9.3	N	N	9.3	56.8	
$2\text{Hg}_2^{2+} + \text{OH}^- = \underline{(\text{Hg}_2)_2(\text{OH})^{3+}}$	11.5	N	N	11.5	479.8	
$\underline{\text{Hg}_2\text{Cl}_2} = \text{Hg}_2^{2+} + 2\text{Cl}^-$	-17.9	N	N	N	211.0	
$\text{Hg}_2^{2+} + n\text{SO}_4^{2-} = \underline{\text{Hg}_2(\text{SO}_4)_n^{2-2n}}, n = 1$ 2	<sup>1</sup> 2.7	N	N	N	606.3	
	<sup>1</sup> 5.3	N	N	N	1,365.7	
$\underline{\text{Hg}_2\text{SO}_4} = \text{Hg}_2^{2+} + \text{SO}_4^{2-}$	-6.1	N	N	N	625.7	
$\underline{\text{Hg}_2\text{CO}_3(\text{s})} = \text{Hg}_2^{2+} + \text{CO}_3^{2-}$	-14.0	N	N	-13.2	454.3	
$\underline{\text{Hg}_2(\text{NCS})_2} = \text{Hg}_2^{2+} + 2\text{NCS}^-$	-19.5	N	N	N	-227.6	

N No data.

<sup>1</sup>Estimated from ionic-strength dependence for corresponding reactions of other divalent metal ions (data given in reference 15 for Hg complexes at ionic strength 0.5M).



Table D-5.--Thermodynamic data for mercury(II) species at 25° C

Reaction	Log K at ionic strength (M)				$-\Delta_f G^\circ$ of underlined species kJ·mol <sup>-1</sup>	Additional references
	0.0	0.1	1.0	3.0		
$\text{Hg}^{2+} + n\text{OH}^- = \underline{\text{Hg}(\text{OH})_n}^{2-n}$ , n = 1	10.6	N	10.1	10.7	53.2	
2	21.8	21.2	21.3	22.2	274.4	
3	20.9	N	N	N	426.6	
4	<sup>1</sup> 18.9	N	N	N	572.5	
$2\text{Hg}^{2+} + \text{OH}^- = \underline{\text{Hg}_2(\text{OH})}^{3+}$	10.7	N	N	11.5	-110.8	
$\underline{\text{HgO}}(\text{s}) + \text{H}_2\text{O} = \text{Hg}^{2+} + 2\text{OH}^-$	-25.4	N	N	-25.6	58.5	
$\text{Hg}^{2+} + n\text{Cl}^- = \underline{\text{HgCl}}_n^{2-n}$ , n = 1	<sup>2</sup> 6.8	N	6.7	7.2	5.4	
2	<sup>2</sup> 13.2	N	13.2	14.0	173.1	
3	<sup>2</sup> 14.0	N	14.2	15.1	308.9	
4	<sup>2</sup> 15.1	N	15.3	16.1	446.4	
$\underline{\text{HgCl}}_2(\text{s}) = \text{HgCl}_2$	<sup>2</sup> -0.9	N	N	N	178.3	
$\text{HgCl}^+ + \text{H}_2\text{O} = \underline{\text{HgCl}}(\text{OH}) + \text{H}^+$	<sup>3</sup> -3.0	N	-3.0	-3.0	225.5	
$\underline{\text{Hg}_3\text{O}_2\text{Cl}_2} = 2\text{HgO}(\text{s}) + \text{HgCl}_2$	<sup>4</sup> -4.2	N	N	N	<sup>4</sup> 314.	
$\underline{\text{Hg}_5\text{O}_4\text{Cl}_2} = 4\text{HgO}(\text{s}) + \text{HgCl}_2$	<sup>4</sup> -6.6	N	N	N	<sup>4</sup> 445.	
$\underline{\text{HgS}}(\text{s}) + 2\text{H}^+ = \text{Hg}^{2+} + \text{H}_2\text{S}$	-32.2	N	N	N	47.	
$\text{Hg}^{2+} + n\text{SH}^- = \underline{\text{Hg}(\text{SH})_n}^{2-n}$ , n = 1	<sup>5</sup> 17.	N	N	N	-79.9	
2	<sup>5</sup> 37.	N	N	N	22.0	
$\text{Hg}(\text{SH})_2 = \underline{\text{HgS}(\text{SH})}^- + \text{H}^+$	<sup>6</sup> -5.	N	-6.2	N	-6.5	
$\text{HgS}(\text{SH})^- = \underline{\text{HgS}_2}^{2-} + \text{H}^+$	<sup>6</sup> -7.	N	-8.3	N	-46.5	
$\text{Hg}^{2+} + n\text{S}_2\text{O}_3^{2-} = \underline{\text{Hg}(\text{S}_2\text{O}_3)_n}^{2-2n}$ , n = 1	<sup>7</sup> 14.	N	N	N	437.8	
2	29.2	N	N	N	1,047.1	
3	30.6	N	N	N	1,577.6	
$2\text{Hg}^{2+} + 2\text{S}_2\text{O}_3^{2-} = \underline{\text{Hg}_2(\text{S}_2\text{O}_3)_2}$	<sup>8</sup> 32.	N	N	N	898.5	
$\text{Hg}^{2+} + n\text{SO}_4^{2-} = \underline{\text{Hg}(\text{SO}_4)_n}^{2-2n}$ , n = 1	<sup>9</sup> 2.7	N	N	N	595.3	
2	<sup>9</sup> 4.2	N	N	N	1,348.4	



Table D-5.-Thermodynamic data for mercury(II) species at 25° C-Continued

Reaction	Log K at ionic strength (M)				$-\Delta_f G^\circ$ of underlined species $\text{kJ}\cdot\text{mol}^{-1}$	Additional references
	0.0	0.1	1.0	3.0		
$\text{Hg}^{2+} + n\text{NH}_3 = \underline{\text{Hg}(\text{NH}_3)_n}^{2+}$ , $n = 1$	9.0	N	N	N	-86.7	
2	17.7	N	N	N	-10.6	
3	18.7	N	N	N	21.6	
4	19.3	N	N	N	51.6	
$\text{Hg}^{2+} + \text{HCO}_3 = \underline{\text{Hg}(\text{HCO}_3)}$	<sup>10</sup> 6.	N	N	5.4	456.5	
$\text{Hg}^{2+} + n\text{CO}_3^{2-} = \underline{\text{Hg}(\text{CO}_3)_n}^{2-2n}$ , $n = 1$	<sup>10</sup> 12.	N	N	11.0	431.9	
$n = 2$	<sup>10</sup> 15.5	N	N	N	979.9	
$\text{HgCO}_3 + \text{H}_2\text{O} = \underline{\text{Hg}(\text{CO}_3)(\text{OH})} + \text{H}^+$	<sup>10</sup> -7.	N	N	6.6	629.2	
$\underline{\text{HgCO}_3(\text{s})} = \text{Hg}^{2+} + \text{CO}_3^{2-}$	<sup>11</sup> -14.	N	N	N	437.6	
$\underline{\text{Hg}_3\text{O}_2(\text{CO}_3)(\text{s})} + 2\text{H}_2\text{O} = 3\text{Hg}^{2+} + 4\text{OH}^- + \text{CO}_3^{2-}$	-67.2	N	N	-67.2	572.6	
$\text{Hg}^{2+} + n\text{NCS}^- = \underline{\text{Hg}(\text{NCS})_n}^{2-n}$ , $n = 1$	<sup>12</sup> 9.2	N	9.1	N	-204.8	
2	17.3	16.4	16.9	N	-251.3	
3	20.0	19.1	19.7	N	-328.5	
4	21.8	21.2	21.7	N	-411.0	
$\underline{\text{Hg}(\text{NCS})_2} = \text{Hg}(\text{NCS})_2$	-2.7	N	-2.7	N	-235.8	
$\text{Hg}(\text{NCS})^+ + \text{H}_2\text{O} = \underline{\text{Hg}(\text{NCS})(\text{OH})} + \text{H}^+$	<sup>3</sup> -3.4	N	-3.4	N	13.0	
$\text{Hg}^{2+} + n\text{CN}^- = \underline{\text{Hg}(\text{CN})_n}^{2-n}$ , $n = 1$	17.0	17.7	N	N	-240.0	
2	32.8	34.1	N	N	-322.2	
3	36.3	37.9	N	N	-474.6	
4	39.0	40.8	N	N	-631.6	
$\underline{\text{Hg}(\text{CN})_2(\text{s})} = \text{Hg}(\text{CN})_2$	-0.4	N	N	N	-319.9	19
$\text{Hg}(\text{CN})_2 + \text{Hg}(\text{OH})_2 = 2\underline{\text{Hg}(\text{OH})(\text{CN})}$	<sup>13</sup> 2.4	N	N	N	-17.0	
$\underline{\text{Hg}_2\text{O}(\text{CN})_2} + \text{H}_2\text{O} = 2\text{Hg}(\text{OH})(\text{CN})$	-1.2	N	N	N	-257.5	19
$\text{Hg}(\text{CN})_2(\text{s}) + \text{OH}^- = \underline{\text{Hg}(\text{OH})(\text{CN})_2}$	0.0	N	N	N	-162.6	22



Table D-5.--Thermodynamic data for mercury(II) species at 25° C--Continued

Reaction	Log K at ionic strength (M)				$-\Delta_f G^\circ$ of underlined species kJ·mol <sup>-1</sup>	Additional references
	0.0	0.1	1.0	3.0		
$\text{Hg}^{2+} + m\text{Cl}^- + n\text{CN}^- =$						
$\text{HgCl}_m(\text{CN})_n$ , $m = 1, n = 1$	<sup>14</sup> 23.5	N	N	N	-71.7	23
1 2	<sup>14</sup> 33.2	N	N	N	-188.7	23
1 3	<sup>14</sup> 36.8	N	N	N	-340.5	23
2 1	<sup>14</sup> 23.8	N	N	N	61.2	23
2 2	<sup>14</sup> 33.6	N	N	N	-55.2	23
3 1	<sup>14</sup> 24.2	N	N	N	194.7	23
$\text{Hg}^{2+} + m\text{NCS}^- + n\text{CN}^- =$						
$\text{Hg}(\text{NCS})_m(\text{CN})_n$ , $m = 1, n = 1$	<sup>15</sup> 24.8	N	N	N	-288.1	24
1 2	<sup>15</sup> 33.6	N	N	N	-410.3	24
1 3	<sup>15</sup> 37.3	N	N	N	-561.6	24
2 1	<sup>15</sup> 26.2	N	N	N	-372.8	24
2 2	<sup>15</sup> 35.0	N	N	N	-495.0	24
3 1	<sup>15</sup> 27.8	N	N	N	-456.4	24

N No data.

<sup>1</sup>Estimated from data for corresponding hydrosulfide complexes.<sup>2</sup>Calculated from Gibbs energy data in reference 1.<sup>3</sup>Estimated assuming zero ionic-strength dependence.<sup>4</sup>Gibbs energy data estimated on basis of data for Br analogs in reference 1, by assuming equal enthalpies of formation from HgO and Hg(II) halide; log K values then calculated.<sup>5</sup>Estimated from data for corresponding halide and NCS<sup>-</sup> complexes.<sup>6</sup>Estimated.<sup>7</sup>Estimated from data for corresponding Zn and Cd complexes, assuming slight instability to disproportionation.<sup>8</sup>Estimated by assuming log K = 4 for reaction  $2\text{Hg}(\text{S}_2\text{O}_3) = \text{Hg}_2(\text{S}_2\text{O}_3)_2$  by comparison with corresponding reactions of Zn and Cd complexes.<sup>9</sup>Estimated from ionic-strength dependence for corresponding reactions of other divalent metal ions (data given in reference 3 for Hg complexes at ionic strength 0.5 M).<sup>10</sup>Estimated from additional data at ionic strength 0.5 M and corresponding data for other divalent metal ions.<sup>11</sup>Estimated by comparison of data for other divalent metal carbonates and lower stability toward decomposition to HgO and CO<sub>2</sub> than Hg<sub>3</sub>O<sub>2</sub>CO<sub>3</sub>.<sup>12</sup>Estimated from ionic-strength dependence for reactions of corresponding halide complexes.



Table D-5.-Thermodynamic data for mercury(II) species at 25° C—Continued

<sup>13</sup>Log K = 2.5 at 30° C and ionic strength 2.0M, and enthalpy change estimated as +5 kcal, from data in reference 3; corrected to 25° C, zero ionic-strength dependence assumed.

<sup>14</sup>Data in reference 23 are log K values for successive replacement of Cl<sup>-</sup> by CN<sup>-</sup> in chloro complexes at ionic strength 2.0M. To estimate values at zero ionic strength, these replacement log K values were multiplied by constant factors for each respective x + y = 2, 3, 4, such that the sum of replacement constants for each value of x + y equaled the difference of the formation log K values of the respective chloro and cyano complexes at zero ionic strength, namely 19.6, 22.3, 23.9 for x + y = 2, 3, 4, respectively. The tabulated formation constants were then calculated from the obtained replacement log K values.

<sup>15</sup>Data in reference 24 are log K values for successive replacement of Br<sup>-</sup> by CN<sup>-</sup> in HgBr<sub>4</sub><sup>2-</sup> at ionic strength 2.0M. Values at zero ionic strength were estimated in the same way as for the corresponding chloro complexes for x + y = 4. For x + y = 2, 3, values were estimated via the trends in the values for the corresponding chloro complexes. The differences of the formation log K values for bromo and cyano complexes are 15.4, 16.7, 18.1 for x + y = 2, 3, 4, respectively. Corresponding differences for thiocyanato and cyano complexes are 15.5, 16.3, 17.2. To estimate the replacement log K values for NCS<sup>-</sup> by CN<sup>-</sup>, the replacement log K values of Br<sup>-</sup> by CN<sup>-</sup> were multiplied by constant factors for each respective x + y = 2, 3, 4, such that the sum of replacement log K values equaled the difference of formation log K values of the respective thiocyanate and cyanide complexes. The tabulated formation constants were then calculated from the obtained replacement log K values.



Table D-6.-Thermodynamic data for copper(I) species at 25° C

Reaction	Log K at ionic strength (M)				$-\Delta_f G^\circ$ of underlined species kJ·mol <sup>-1</sup>	Additional references
	0.0	0.1	1.0	3.0		
$\text{Cu}^+ + n\text{OH}^- = \underline{\text{Cu}(\text{OH})_n}^{1-n}, n = 1$	<sup>1</sup> 4.5	N	N	N	134.1	
2	<sup>1</sup> 9.7	N	N	N	321.1	
$\underline{\text{Cu}_2\text{O}(\text{s})} + \text{H}_2\text{O} = 2\text{Cu}^+ + 2\text{OH}^-$	-29.5	N	N	N	148.	
$\text{Cu}^+ + n\text{Cl}^- = \underline{\text{CuCl}}_n^{1-n}, n = 1$	<sup>2</sup> 2.7	N	N	N	97.7	
2	5.5	N	5.2	5.5	244.9	
3	5.7	N	N	5.2	377.2	
4	<sup>2</sup> 5.7	N	N	N	508.4	
$\underline{\text{CuCl}} = \text{Cu}^+ + \text{Cl}^-$	-6.7	N	N	N	120.5	
$\underline{\text{Cu}_2\text{S}(\text{s})} + 2\text{H}^+ = 2\text{Cu}^+ + \text{H}_2\text{S}$	-26.3	N	N	N	80.	
$\text{Cu}^+ + n\text{SH}^- = \underline{\text{Cu}(\text{SH})_n}^{1-n}, n = 1$	<sup>3</sup> 14.	N	N	N	18.7	
2	<sup>3</sup> 16.	N	N	N	17.8	
$\text{CuSH} = \underline{\text{CuS}^-} + \text{H}^+$	<sup>4</sup> 8.	N	N	N	-27.0	
$\text{Cu}(\text{SH})_2^- = \underline{\text{CuS}(\text{SH})_2^{2-}} + \text{H}^+$	<sup>4</sup> 9.	N	N	N	-33.5	
$2\text{Cu}^+ + 3\text{SH}^- + \text{OH}^- = \underline{\text{Cu}_2\text{S}(\text{SH})_2^{2-}} + \text{H}_2\text{O}$	<sup>3</sup> 42.	N	N	N	25.1	
$\text{Cu}^+ + n\text{S}_2\text{O}_3^{2-} = \underline{\text{Cu}(\text{S}_2\text{O}_3)_n}^{1-2n}, n = 1$	<sup>5</sup> 11.0	N	10.3	N	536.4	
2	<sup>5</sup> 13.0	N	12.2	N	1,070.3	
3	<sup>5</sup> 14.7	N	13.5	N	1,602.5	
$\text{Cu}^+ + \text{SO}_4^{2-} = \underline{\text{Cu}(\text{SO}_4)}^{1-}$	<sup>6</sup> 1.	N	N	N	701.3	
$\text{Cu}^+ + n\text{NH}_3 = \underline{\text{Cu}(\text{NH}_3)_n}^{1+}, n = 1$	5.8	N	N	N	10.7	
2	10.6	N	N	N	64.6	
$\text{Cu}^+ + n\text{NCS}^- = \underline{\text{Cu}(\text{NCS})_n}^{1-n}, n = 1$	<sup>7</sup> 5.	N	N	N	-113.1	
2	<sup>7</sup> 11.	N	N	N	-171.5	
3	<sup>7</sup> 11.	N	N	N	-264.2	
4	<sup>7</sup> 11.	N	N	N	-356.9	
$\underline{\text{CuNCS}} = \text{Cu}^+ + \text{NCS}^-$	<sup>7</sup> 13.	N	N	N	-67.4	



Table D-6.-Thermodynamic data for copper(I) species at 25° C-Continued

Reaction	Log K at ionic strength (M)				$-\Delta_f G^\circ$ of underlined species kJ·mol <sup>-1</sup>	Additional references
	0.0	0.1	1.0	3.0		
$\text{Cu}^+ + n\text{CN}^- = \underline{\text{Cu}(\text{CN})_n}^{1-n}$ , n = 1	<sup>8</sup> 10.5	N	N	N	-161.4	28
2	21.7	N	N	N	-269.8	
3	27.0	N	N	N	-412.0	
4	28.5	N	N	N	-575.8	
$\underline{\text{Cu}(\text{CN})_2(\text{s})} = \text{Cu}^+ + \text{CN}^-$	-19.5	N	N	N	-110.0	
$\text{Cu}^+ + \text{CN}^- + \text{OH}^- = \underline{\text{Cu}(\text{CN})(\text{OH})^-}$	<sup>9</sup> 14.7	N	N	N	19.9	

N No data.

<sup>1</sup>Estimated via trends in corresponding Zn, Cd, Hg complexes.

<sup>2</sup>Estimated via trends in corresponding Ag complexes.

<sup>3</sup>Estimated via trends in corresponding Ag and Au complexes and analogous halide and SCN<sup>-</sup> complexes.

<sup>4</sup>Assumed similar to values for corresponding Ag complexes.

<sup>5</sup>Estimated from ionic-strength dependence for reactions of corresponding Ag complexes.

<sup>6</sup>Estimated via comparison of corresponding Ag and Tl complexes.

<sup>7</sup>Estimated from ionic-strength dependence for reactions of corresponding Ag complexes (data given in reference 3 for ionic strength 0.5M).

<sup>8</sup>Derived from estimate of log K = -9 for  $\text{CuCN}(\text{s}) = \text{CuCN}$ .

<sup>9</sup>Derived from estimate of log K = -2 for  $\text{Cu}(\text{CN})_2^- + \text{Cu}(\text{OH})_2^- = 2\text{Cu}(\text{CN})(\text{OH})^-$  (log K = +1.5 for corresponding reaction of Ag complexes).



Table D-7.--Thermodynamic data for copper(II) species at 25° C

Reaction	Log K at ionic strength (M)				$-\Delta_f G^\circ$ of underlined species kJ·mol <sup>-1</sup>	Additional references
	0.0	0.1	1.0	3.0		
$\text{Cu}^{2+} + n\text{OH}^- = \underline{\text{Cu}(\text{OH})_n}^{2-n}$ , n = 1	6.5	6.1	N	6.8	129.2	
2	11.8	N	12.8	N	316.8	
3	15.0	N	14.5	N	492.3	
4	16.4	N	15.6	N	657.6	
$2\text{Cu}^{2+} + 2\text{OH}^- = \underline{\text{Cu}_2(\text{OH})_2}^{2+}$	17.4	16.8	17.0	17.6	283.5	
$3\text{Cu}^{2+} + 4\text{OH}^- = \underline{\text{Cu}_3(\text{OH})_4}^{2+}$	35.2	33.5	N	N	634.5	
$\underline{\text{CuO}}(\text{s}) + \text{H}_2\text{O} = \text{Cu}^{2+} + 2\text{OH}^-$	-20.3	N	N	N	128.	
$\underline{\text{Cu}(\text{OH})_2}(\text{cr}) = \text{Cu}^{2+} + 2\text{OH}^-$	-19.3	N	N	N	359.6	
$\underline{\text{Cu}(\text{OH})_2}(\text{am}) = \text{Cu}^{2+} + 2\text{OH}^-$	-18.8	N	N	N	356.7	
$\text{Cu}^{2+} + n\text{Cl}^- = \underline{\text{CuCl}_n}^{2-n}$ , n = 1	.2	N	-.2	.0	67.1	
2	.0	N	-.5	-.4	197.2	
$\underline{\text{Cu}_2(\text{OH})_3\text{Cl}} = 2\text{Cu}^{2+} + 3\text{OH}^- + \text{Cl}^-$	-34.6	N	-34.3	N	670.2	
$\underline{\text{CuS}}(\text{s}) + 2\text{H}^+ = \text{Cu}^{2+} + \text{H}_2\text{S}$	-16.4	N	N	N	56.	
$\text{Cu}^{2+} + n\text{SO}_4^{2-} = \underline{\text{Cu}(\text{SO}_4)_n}^{2-2n}$ , n = 1	2.3	N	.8	.5	692.4	
$\underline{\text{Cu}_4(\text{OH})_6(\text{SO}_4)}(\text{s}) = 4\text{Cu}^{2+} + 6\text{OH}^- + \text{SO}_4^{2-}$	-68.6	N	-67.4	N	1,504.5	
$\text{Cu}^{2+} + n\text{NH}_3 = \underline{\text{Cu}(\text{NH}_3)_n}^{2+}$ , n = 1	4.0	N	4.1	N	-15.9	
2	7.5	N	7.6	N	30.6	
3	10.3	N	10.5	N	73.1	
4	11.8	N	12.6	N	108.2	
$\text{Cu}^{2+} + \text{HCO}_3^- = \underline{\text{Cu}(\text{HCO}_3)}^+$	1.8	N	1.0	N	532.0	



Table D-7.-Thermodynamic data for copper(II) species at 25° C-Continued

Reaction	Log K at ionic strength (M)				$-\Delta_f G^\circ$ of underlined species kJ·mol <sup>-1</sup>	Additional references
	0.0	0.1	1.0	3.0		
$\text{Cu}^{2+} + n\text{CO}_3^{2-} = \underline{\text{Cu}(\text{CO}_3)_n}^{2-2n}, n = 1$	6.8	N	5.7	N	501.6	29
$n = 2$	10.2	N	9.3	N	1,049.0	
$\underline{\text{CuCO}_3(\text{s})} = \text{Cu}^{2+} + \text{CO}_3^{2-}$	<sup>1</sup> -11.0	N	N	N	525.6	
$\underline{\text{Cu}_2(\text{OH})_2(\text{CO}_3)(\text{s})} = 2\text{Cu}^{2+} + 2\text{OH}^- + \text{CO}_3^{2-}$	-33.3	N	N	N	902.3	
$\underline{\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2(\text{s})} = 3\text{Cu}^{2+} + 2\text{OH}^-$						
$+ 2\text{CO}_3^{2-}$	-44.9	N	N	N	1,431.3	
$\text{Cu}^{2+} + n\text{NCS}^- = \underline{\text{Cu}(\text{NCS})_n}^{2-n}, n = 1$	2.3	1.9	1.7	1.9	-144.8	
$2$	3.6	3.0	2.7	N	-230.1	
$\text{Cu}^{2+} + n\text{CN}^- = \underline{\text{Cu}(\text{CN})_n}^{2-n}, n = 4$	<sup>2</sup> 22.2	N	N	N	-627.9	
$2\underline{\text{Cu}(\text{CN})_2(\text{s})} = \text{Cu}^{2+} + \text{Cu}(\text{CN})_4^{2-}$	<sup>3</sup> -10.	N	N	N	-318.1	
$\underline{\text{Cu}_3(\text{CN})_4(\text{s})} = \text{Cu}^{2+} + 2\text{Cu}(\text{CN})_2^-$	<sup>4</sup> -15.				-519.2	

N No data.

<sup>1</sup>Estimated from data for carbonates of other divalent metal ions, consistent with the stability of the hydroxide carbonates.<sup>2</sup>Calculated from reduction potential of +0.54 V to  $\text{Cu}(\text{CN})_4^{3-}$  in reference 29 and data for Cu(I) complexes.<sup>3</sup>Estimated from data for cyanides of Ni and Zn.<sup>4</sup>Estimated assuming a solubility of about  $10^{-5}$  M and stability with respect to disproportionation to CuCN and  $\text{Cu}(\text{CN})_2$ .



Table D-8.-Thermodynamic data for silver(I) species at 25° C

Reaction	Log K at ionic strength (M)				$-\Delta_f G^\circ$ of underlined species kJ·mol <sup>-1</sup>	Additional references
	0.0	0.1	1.0	3.0		
$\text{Ag}^+ + n\text{OH}^- = \underline{\text{Ag}(\text{OH})_n}^{1-n}, n = 1$	2.0	N	N	N	91.6	
2	4.0	N	N	3.6	260.3	
$\underline{\text{Ag}_2\text{O}(\text{s})} + \text{H}_2\text{O} = 2\text{Ag}^+ + 2\text{OH}^-$	-15.4	-15.2	-14.4	-14.8	11.3	
$\text{Ag}^+ + n\text{Cl}^- = \underline{\text{AgCl}}_n^{1-n}, n = 1$	3.3	3.1	3.4	<sup>1</sup> 3.3	72.9	
2	5.2	5.1	5.2	<sup>1</sup> 5.6	215.0	
3	5.2	N	N	<sup>1</sup> 5.5	346.2	
4	5.2	N	N	<sup>1</sup> 5.6	477.4	
$\underline{\text{AgCl}} = \text{Ag}^+ + \text{Cl}^-$	-9.7	N	-9.7	-10.0	109.8	
$\underline{\text{Ag}_2\text{S}(\text{s})} + 2\text{H}^+ = 2\text{Ag}^+ + \text{H}_2\text{S}$	-29.0	N	N	N	39.	
$\text{Ag}^+ + n\text{SH}^- = \underline{\text{Ag}(\text{SH})_n}^{1-n}, n = 1$	16.2	13.6	13.3	N	3.1	30
2	18.0	17.7	17.2	N	1.0	30
$\text{AgSH} = \underline{\text{AgS}^-} + \text{H}^+$	<sup>2</sup> 8.3	8.3	N	N	-44.3	30
$\text{Ag}(\text{SH})_2^- = \underline{\text{AgS}(\text{SH})^{2-}} + \text{H}^+$	<sup>2</sup> 9.5	9.5	N	N	-53.2	30
$2\text{Ag}^+ + 3\text{SH}^- + \text{OH}^- = \underline{\text{Ag}_2\text{S}(\text{SH})_2^{2-}} + \text{H}_2\text{O}$	<sup>3</sup> 46.	N	44.7	N	-8.4	30
$\text{Ag}^+ + n\text{S}_2\text{O}_3^{2-} = \underline{\text{Ag}(\text{S}_2\text{O}_3)_n}^{1-2n}, n = 1$	8.7	N	N	N	495.1	
2	13.4	N	12.5	12.8	1,044.4	
3	14.0	N	12.8	13.3	1,570.3	
$\text{Ag}^+ + \text{SO}_4^{2-} = \underline{\text{Ag}(\text{SO}_4)^-}$	1.3	N	.3	0.2	674.8	
$\text{Ag}^+ + n\text{NH}_3 = \underline{\text{Ag}(\text{NH}_3)_n}^+, n = 1$	3.3	N	3.3	3.5	-31.8	
2	7.2	N	7.4	7.6	17.0	
$\underline{\text{Ag}_2\text{CO}_3} = 2\text{Ag}^+ + \text{CO}_3^{2-}$	-11.1	N	N	N	437.2	
$\text{Ag}^+ + n\text{NCS}^- = \underline{\text{Ag}(\text{NCS})_n}^{1-n}, n = 1$	4.8	4.6	N	<sup>1</sup> 4.6	-142.4	
2	8.2	8.1	N	<sup>1</sup> 8.2	-215.7	
3	9.5	9.3	N	<sup>1</sup> 9.5	-301.0	
4	9.7	10.5	N	<sup>1</sup> 10.5	-392.5	



Table D-8.-Thermodynamic data for silver(I) species at 25° C-Continued

Reaction	Log K at ionic strength (M)				$-\Delta_f G^\circ$ of underlined species $\text{kJ}\cdot\text{mol}^{-1}$	Additional references
	0.0	0.1	1.0	3.0		
$\text{AgNCS} = \text{Ag}^+ + \text{NCS}^-$	-12.0	-11.8	N	N	-101.3	
$\text{Ag}^+ + n\text{CN}^- = \underline{\text{Ag}(\text{CN})_n}^{1-n}$ , $n = 1$	<sup>4</sup> 9.7	N	N	N	-194.1	
2	20.5	20.0	20.0	N	-304.9	
3	21.4	N	20.7	N	-472.1	
4	<sup>5</sup> 21.4	N	21.2	N	-644.5	
$\underline{\text{Ag}(\text{CN})(\text{s})} = \text{Ag}^+ + \text{CN}^-$	-15.7	-15.2	-15.4	N	-159.9	
$\text{Ag}^+ + \text{CN}^- + \text{OH}^- = \underline{\text{Ag}(\text{CN})(\text{OH})^-}$	13.2	N	12.7	N	-16.9	

N No data.

<sup>1</sup>Interpolated.<sup>2</sup>Estimated.<sup>3</sup>Derived by assuming zero ionic-strength dependence of the reaction  $2\text{Ag}(\text{SH})_2^- = \text{Ag}_2\text{S}(\text{SH})_2^{2-} + \text{H}_2\text{S}$ .<sup>4</sup>Derived from estimate of  $\log K = -6$  for  $\text{AgCN}(\text{s}) = \text{AgCN}$ .<sup>5</sup>Estimated via trends in corresponding halide and  $\text{NCS}^-$  complexes.



Table D-9.-Thermodynamic data for gold(I) species at 25° C

Reaction	Log K at ionic strength (M)				$-\Delta_f G^\circ$ of underlined species $\text{kJ}\cdot\text{mol}^{-1}$	Additional references
	0.0	0.1	1.0	3.0		
$\text{Au}^+ + n\text{OH}^- = \underline{\text{Au}(\text{OH})_n}^{1-n}$ , $n = 1$	<sup>1</sup> 10.	N	N	N	50.4	
	<sup>2</sup> 22.	N	N	N	276.2	33
$\underline{\text{Au}_2\text{O}(\text{s})} + \text{H}_2\text{O} = 2\text{Au}^+ + 2\text{OH}^-$	-19.5	N	N	N	<sup>3</sup> -28.	
$\text{Au}^+ + n\text{Cl}^- = \underline{\text{AuCl}_n}^{1-n}$ , $n = 1$	<sup>1</sup> 4.5	N	N	N	-7.1	
	<sup>2</sup> 9.3	N	N	N	151.5	31
$\text{AuCl}_2^- + \text{OH}^- = \underline{\text{Au}(\text{OH})\text{Cl}}^{1-} + \text{Cl}^-$	6.7	N	N	N	215.8	33
$\underline{\text{AuCl}} = \text{Au}^+ + \text{Cl}^-$	-8.9	N	N	N	<sup>4</sup> 18.	
$\underline{\text{Au}_2\text{S}(\text{s})} + 2\text{H}^+ = 2\text{Au}^+ + \text{H}_2\text{S}$	-47.7	N	N	N	-28.	34
$\text{Au}^+ + n\text{SH}^- = \underline{\text{Au}(\text{SH})_n}^{1-n}$ , $n = 1$	20.	N	N	N	-62.1	30
	33.	N	N	N	-.2	30
$\text{AuSH} = \underline{\text{AuS}^-} + \text{H}^+$	<sup>5</sup> 6.	N	N	N	-96.4	30
$\text{Au}(\text{SH})_2^- = \underline{\text{AuS}(\text{SH})}^{2-} + \text{H}^+$	<sup>5</sup> 8.	N	N	N	-45.9	30
$2\text{Au}^+ + 3\text{SH}^- + \text{OH}^- = \underline{\text{Au}_2\text{S}(\text{SH})_2}^{2-} + \text{H}_2\text{O}$	73.	N	N	N	-28.1	30
$\text{Au}^+ + n\text{S}_2\text{O}_3^{2-} = \underline{\text{Au}(\text{S}_2\text{O}_3)_n}^{1-2n}$ , $n = 1$	<sup>1</sup> 18.	N	N	N	461.2	
	<sup>2</sup> 26.2	N	N	N	1030.5	31
$\text{Au}^+ + \text{SO}_4^{2-} = \underline{\text{Au}(\text{SO}_4)}^-$	<sup>6</sup> 1.	N	N	N	586.2	
$\text{Au}^+ + n\text{NH}_3 = \underline{\text{Au}(\text{NH}_3)_n}^+$ , $n = 1$	<sup>1</sup> 8.	N	N	N	-91.8	
	<sup>2</sup> 19.3	N	N	N	-1.0	31, 35
$\text{Au}^+ + n\text{NCS}^- = \underline{\text{Au}(\text{NCS})_n}^{1-n}$ , $n = 1$	<sup>1</sup> 8.5	N	N	N	-208.2	
	<sup>2</sup> 17.6	N	N	N	-248.9	31
$\text{Au}(\text{NCS})_2^- + \text{OH}^- = \underline{\text{Au}(\text{OH})(\text{NCS})}^- + \text{NCS}^-$	2.5	N	N	N	15.3	33
$\underline{\text{AuNCS}} = \text{Au}^+ + \text{NCS}^-$	<sup>7</sup> -14.				-176.8	



Table D-9.--Thermodynamic data for gold(I) species at 25° C--Continued

Reaction	Log K at ionic strength (M)				$-\Delta_f G^\circ$ of underlined species $\text{kJ}\cdot\text{mol}^{-1}$	Additional references
	0.0	0.1	1.0	3.0		
$\text{Au}^+ + n\text{CN}^- = \underline{\text{Au}(\text{CN})_n}^{1-n}$ , $n = 1$	<sup>8</sup> 18.	N	N	N	-233.7	
	<sup>2</sup> 37.0	N	N	N	-297.6	31
$\underline{\text{Au}(\text{CN})_2(\text{s})} = \text{Au}^+ + \text{CN}^-$	<sup>9</sup> -32.	N	N	N	-153.7	36
$\text{Au}^+ + \text{CN}^- + \text{OH}^- = \underline{\text{Au}(\text{CN})(\text{OH})}^-$	<sup>8</sup> 30.	N	N	N	-7.9	

N No data.

<sup>1</sup>Estimated via trends in Zn, Cd, Hg complexes versus values for Cu, Ag complexes.

<sup>2</sup>Calculated from difference of reduction potentials of uncomplexed  $\text{Au}^+$  and the complex.

<sup>3</sup>Estimated assuming slightly unstable to disproportionation to Au and  $\text{Au}_2\text{O}_3$ .

<sup>4</sup>Estimated from standard enthalpy of formation and data for AgCl.

<sup>5</sup>Assumed 2 log K units more acidic than corresponding Ag complexes.

<sup>6</sup>Estimated from comparison of corresponding Ag, Tl complexes.

<sup>7</sup>Estimated from values for Au halides and corresponding Ag compounds (values for AuBr and AuI estimated in same way as AuCl).

<sup>8</sup>Estimated log K = +1 for  $\text{Au}(\text{CN})_2^- + \text{Au}(\text{OH})_2^- = 2\text{Au}(\text{CN})(\text{OH})^-$  from values for corresponding reactions for halide and  $\text{NCS}^-$  complexes and corresponding reactions of analogous Hg(II) complexes; estimated log K = 12 for  $\text{AuCN} + \text{OH}^- = \text{Au}(\text{CN})(\text{OH})^-$  in the same way; tabulated values then calculated.

<sup>9</sup>Derived from estimate of log K = +5 for  $\text{AuCN}(\text{s}) + \text{CN}^- = \text{Au}(\text{CN})_2^{1-}$  suggested by information in reference 36.



Table D-10.--Thermodynamic data for gold(III) species at 25° C

Reaction	Log K at ionic strength ( <u>M</u> )				$-\Delta_f G^\circ$ of underlined species kJ·mol <sup>-1</sup>	Additional references
	0.0	0.1	1.0	3.0		
$\text{Au}^{3+} + n\text{OH}^- = \underline{\text{Au}(\text{OH})_n}^{3-n}$ , $n = 1$	<sup>1</sup> 15.	N	N	N	-191.3	
2	<sup>1</sup> 29.7	N	N	N	49.9	
3	43.7	N	N	N	287.4	
4	<sup>2</sup> 51.7	N	N	N	490.2	31
$\underline{\text{Au}_2\text{O}_3(\text{s})} + 3\text{H}_2\text{O} = 2\text{Au}(\text{OH})_3$	-11.0	N	N	N	-74.	37, 38
$\text{Au}^{3+} + n\text{Cl}^- = \underline{\text{AuCl}_n}^{3-n}$ , $n = 3$	20.3	N	N	N	75.6	
4	<sup>2</sup> 25.3	N	N	N	235.3	31
$\text{AuCl}_3 + \text{H}_2\text{O} = \underline{\text{AuCl}_3(\text{OH})}^- + \text{H}^+$	-1.0	N	-0.6	N	307.1	
$\text{AuCl}_{4-n}(\text{OH})_n^- + \text{OH}^- =$ $\underline{\text{AuCl}_{3-n}(\text{OH})_{n+1}}^- + \text{Cl}^-$ , $n = 0$	8.0	N	N	N	307.1	
1	7.0	N	N	N	373.1	
2	6.0	N	N	N	433.5	
$\text{Au}^{3+} + n\text{NH}_3 = \underline{\text{Au}(\text{NH}_3)_n}^{3+}$ , $n = 3$	<sup>1</sup> 49.5	N	N	N	-71.9	39
4	<sup>2</sup> 59.8	N	N	N	13.4	31, 39
$\text{Au}(\text{NH}_3)_3^{3+} + \text{H}_2\text{O} = \underline{\text{Au}(\text{NH}_3)_3(\text{OH})}^{2+} + \text{H}^+$	<sup>1</sup> -1.	N	-0.7	N	171.0	39
$\text{Au}(\text{NH}_3)_4^{3+} = \underline{\text{Au}(\text{NH}_3)_3(\text{NH}_2)}^{2+} + \text{H}^+$	<sup>1</sup> -7.	N	-7.5	N	-26.6	39
$\text{Au}^{3+} + n\text{NCS}^- = \underline{\text{Au}(\text{NCS})_n}^{3-n}$ , $n = 3$	<sup>3</sup> 33.1	N	N	N	-523.3	
4	<sup>2</sup> 43.6	N	N	N	-556.1	31
$\text{Au}(\text{NCS})_3 + \text{H}_2\text{O} = \underline{\text{Au}(\text{NCS})_3(\text{OH})}^{1-} + \text{H}^+$	<sup>3</sup> -1.	N	N	N	231.0	







Table D-11.--Thermodynamic data for nickel(II) species at 25° C

Reaction	Log K at ionic strength (M)				$-\Delta_f G^\circ$ of underlined species kJ·mol <sup>-1</sup>	Additional references
	0.0	0.1	1.0	3.0		
$\text{Ni}^{2+} + n\text{OH}^- = \underline{\text{Ni}(\text{OH})_n}^{2-n}, n = 1$	4.1	3.6	3.7	N	225.1	
2	9.	N	N	N	410.4	
3	12.	N	N	N	584.8	
4	<sup>1</sup> 11.	N	N	N	736.4	
$\underline{\text{NiO}}(\text{s}) + \text{H}_2\text{O} = \text{Ni}^{2+} + 2\text{OH}^-$	-15.9	N	N	N	212.	
$\underline{\text{Ni}(\text{OH})_2}(\text{cr}) = \text{Ni}^{2+} + 2\text{OH}^-$	-17.2	N	N	N	457.2	
$\underline{\text{Ni}(\text{OH})_2}(\text{am}) = \text{Ni}^{2+} + 2\text{OH}^-$	-15.2	N	N	N	445.8	
$\text{Ni}^{2+} + n\text{Cl}^- = \underline{\text{NiCl}_n}^{2-n}, n = 1$	<sup>1</sup> 3	N	.0	-.6	177.3	
$\underline{\text{NiS}}(\text{s}) + 2\text{H}^+ = \text{Ni}^{2+} + \text{H}_2\text{S}$	-3.1	N	N	N	90.	
$\text{Ni}^{2+} + n\text{SO}_4^{2-} = \underline{\text{Ni}(\text{SO}_4)_n}^{2-2n}, n = 1$	2.3	1.0	.7	.3	802.0	
$\text{Ni}^{2+} + n\text{NH}_3 = \underline{\text{Ni}(\text{NH}_3)_n}^{2+}, n = 1$	2.7	2.7	2.8	N	86.3	
2	4.9	4.9	5.0	N	125.4	
3	6.6	N	6.7	N	161.6	
4	7.7	N	7.8	N	194.4	
5	8.3	N	N	N	224.3	
6	8.3	N	N	N	250.8	
$\text{Ni}^{2+} + \text{HCO}_3^- = \underline{\text{Ni}(\text{HCO}_3)}^+$	2.4	N	N	N	645.0	
$\text{Ni}^{2+} + n\text{CO}_3^{2-} = \underline{\text{Ni}(\text{CO}_3)_n}^{2-2n}, n = 1$	<sup>2</sup> 4.5	N	N	N	598.1	
n = 2	<sup>1</sup> 7.5	N	N	N	1143.2	



Table D-11.-Thermodynamic data for nickel(II) species at 25° C—Continued

Reaction	Log K at ionic strength ( <u>M</u> )				$-\Delta_f G^\circ$ of underlined species kJ·mol <sup>-1</sup>	Additional references
	0.0	0.1	1.0	3.0		
<u>NiCO<sub>3</sub>(s)</u> = Ni <sup>2+</sup> + CO <sub>3</sub> <sup>2-</sup>	-11.0	N	N	N	635.2    40	
Ni <sup>2+</sup> + nNCS <sup>-</sup> = <u>Ni(NCS)<sub>n</sub></u> <sup>2-n</sup> , n = 1	1.8	1.3	1.1	1.3	-38.0	
2	<sup>1</sup> 2.5	N	1.6	N	-126.7	
Ni <sup>2+</sup> + nCN <sup>-</sup> = <u>Ni(CN)<sub>n</sub></u> <sup>2-n</sup> , n = 4	30.2	30.5	N	31.1	-472.8	
5	<sup>3</sup> 29.2	N	N	30.4	-650.9	
<u>Ni(CN)<sub>2</sub>(s)</u> = Ni <sup>2+</sup> + 2CN <sup>-</sup>	-19.5	N	N	N	-189.1    41	

N No data.

<sup>1</sup>Estimated from data for corresponding species of other divalent metal ions.<sup>2</sup>Estimated from data at ionic strength 0.7M and data for corresponding complexes of other divalent metal ions.<sup>3</sup>Estimated from data for equally charged Ag(I) complexes.



Table D-12.--Thermodynamic data for cobalt(II) species at 25° C

Reaction	Log K at ionic strength (M)				$-\Delta_f G^\circ$ of underlined species kJ·mol <sup>-1</sup>	Additional references
	0.0	0.1	1.0	3.0		
$\text{Co}^{2+} + n\text{OH}^- = \underline{\text{Co}(\text{OH})_n}^{2-n}$ , n = 1	4.3	N	4.0	4.0	237.6	
2	9.2	N	8.7	N	422.9	
3	10.5	N	9.9	N	587.6	
4	9.7	N	N	N	740.4	
$\underline{\text{CoO}}(\text{s}) + \text{H}_2\text{O} = \text{Co}^{2+} + 2\text{OH}^-$	-13.8	N	N	N	214.	
$\underline{\text{Co}(\text{OH})_2}(\text{cr}) = \text{Co}^{2+} + 2\text{OH}^-$	-15.7	N	N	N	460.0	
$\underline{\text{Co}(\text{OH})_2}(\text{am}) = \text{Co}^{2+} + 2\text{OH}^-$	-14.9	N	N	N	452.0	
$\text{Co}^{2+} + n\text{Cl}^- = \underline{\text{CoCl}_n}^{2-n}$ , n = 1	1.3	N	.0	-.2	188.7	
$\underline{\text{CoS}}(\text{s}) + 2\text{H}^+ = \text{Co}^{2+} + \text{H}_2\text{S}$	-2.2	N	N	N	96.	
$\text{Co}^{2+} + n\text{SO}_4^{2-} = \underline{\text{Co}(\text{SO}_4)_n}^{2-2n}$ , n = 1	2.3	N	.7	.2	813.4	
$\text{Co}^{2+} + n\text{NH}_3 = \underline{\text{Co}(\text{NH}_3)_n}^{2+}$ , n = 1	<sup>2</sup> 2.0	2.1	N	N	93.7	
2	<sup>2</sup> 3.4	N	N	N	128.2	
3	<sup>2</sup> 4.3	N	N	N	159.8	
4	<sup>2</sup> 5.0	N	N	N	190.3	
5	<sup>2</sup> 4.9	N	N	N	216.3	
6	<sup>2</sup> 4.2	N	N	N	238.8	
$\text{Co}^{2+} + \text{HCO}_3^- = \underline{\text{Co}(\text{HCO}_3)}^+$	2.2	N	N	N	655.3	
$\text{Co}^{2+} + n\text{CO}_3^{2-} = \underline{\text{Co}(\text{CO}_3)_n}^{2-2n}$ , n = 1	<sup>3</sup> 4.0	N	N	N	606.6	
n = 2	<sup>1</sup> 6.5	N	N	N	1,148.9	
$\underline{\text{CoCO}_3}(\text{s}) = \text{Co}^{2+} + \text{CO}_3^{2-}$	-10.0	N	N	N	640.9	



Table D-12.-Thermodynamic data for cobalt(II) species at 25° C-Continued

Reaction	Log K at ionic strength (M)				$-\Delta_f G^\circ$ of underlined species $\text{kJ}\cdot\text{mol}^{-1}$	Additional references
	0.0	0.1	1.0	3.0		
$\text{Co}^{2+} + n\text{NCS}^- = \underline{\text{Co}(\text{NCS})_n^{2-n}}$ , $n = 1$ 2	1.7 1 <sup>2</sup> 2.2	1.4 2.0	1.0 1.3	1.3 1.5	-27.2 -117.0	
$\text{Co}^{2+} + n\text{CN}^- = \underline{\text{Co}(\text{CN})_n^{2-n}}$ , $n = 5$	<sup>4</sup> 23.	N	23.0	N	-674.9	43
$\underline{\text{Co}(\text{CN})_2(\text{s})} = \text{Co}^{2+} + 2\text{CN}^-$	<sup>5</sup> -18.	N	N	N	-186.3	
$2\text{Co}(\text{CN})_5^{3-} + \text{H}_2(\text{g}) = 2\underline{\text{CoH}(\text{CN})_5^{3-}}$	1.9	1.9	1.9	2.2	-664.1	44

N No data.

<sup>1</sup>Estimated from data for corresponding complexes of other divalent metal ions.

<sup>2</sup>Corrected to 25° C with enthalpy data estimated from data for corresponding Ni(II) and Cu(II) complexes.

<sup>3</sup>Estimated from data at ionic strength 0.7M and data for corresponding complexes of other divalent metal ions.

<sup>4</sup>Reaction of Co(II) aminopolycarbonxylate complexes with cyanide indicates  $\log K > 20$  (reference 10).

<sup>5</sup>Estimated from data for cyanides of other divalent metal ions.



Table D-13.-Thermodynamic data for cobalt(III) species at 25° C

Reaction	Log K at ionic strength ( <u>M</u> )				$-\Delta_f G^\circ$ of underlined species kJ·mol <sup>-1</sup>	Additional references
	0.0	0.1	1.0	3.0		
$\text{Co}^{3+} + n\text{OH}^- = \underline{\text{Co}(\text{OH})_n}^{3-n}$ , $n = 1$	<sup>1</sup> 13.	N	N	13.5	105.9	
2	<sup>1</sup> 25.	N	N	N	331.7	
3	<sup>1</sup> 34.	N	N	N	540.4	
4	<sup>1</sup> 39.	N	N	N	726.2	
$2\text{Co}^{3+} + 2\text{OH}^- = \underline{\text{Co}_2(\text{OH})_2}^{4+}$	<sup>1</sup> 31.	N	N	N	240.3	
$\underline{\text{CoO}(\text{OH})}(\text{s}) + \text{H}_2\text{O} = \text{Co}^{3+} + 3\text{OH}^-$	-48.5	N	N	N	386.	45
$\underline{\text{Co}(\text{OH})_3}(\text{aged}) = \text{Co}^{3+} + 3\text{OH}^-$	<sup>1</sup> -46.	N	N	N	608.9	
$\underline{\text{Co}(\text{OH})_3}(\text{fresh}) = \text{Co}^{3+} + 3\text{OH}^-$	<sup>1</sup> -44.	N	N	N	597.5	
$\underline{\text{Co}_3\text{O}_4}(\text{s}) + 2\text{H}_2\text{O} = 2\text{CoO}(\text{OH})(\text{s})$ + $\text{Co}^{2+} + 2\text{OH}^-$	-23.5	N	N	N	802.	
$\text{Co}^{3+} + n\text{Cl}^- = \underline{\text{CoCl}_n}^{3-n}$ , $n = 1$	<sup>1</sup> 2.1	N	N	1.4	17.6	
2	<sup>1</sup> 2.9	N	N	N	153.4	
$\text{Co}^{3+} + n\text{SO}_4^{2-} = \underline{\text{Co}(\text{SO}_4)_n}^{3-2n}$ , $n = 1$	<sup>1</sup> 4.0	N	N	N	641.7	
2	<sup>1</sup> 5.4	N	N	N	1,394.2	
$\text{Co}^{3+} + n\text{NH}_3 = \underline{\text{Co}(\text{NH}_3)_n}^{3+}$ , $n = 4$ cis	<sup>2</sup> 25.0	N	N	N	123.1	46
4tr	<sup>2</sup> 23.4	N	N	N	114.0	46
5	<sup>2</sup> 29.8	N	N	N	177.0	
6	<sup>2</sup> 34.	N	N	N	227.5	
$\text{Co}(\text{NH}_3)_4^{3+} + \text{H}_2\text{O} = \underline{\text{Co}(\text{NH}_3)_4(\text{OH})}^{2+}$ + $\text{H}^+$ cis	<sup>3</sup> -5.4	-5.7	<sup>4</sup> -5.9	N	329.5	46, 47, 48, 49
trans	<sup>3</sup> -4.3	N	<sup>4</sup> -4.8	N	326.6	46, 48, 49
$\text{Co}(\text{NH}_3)_4(\text{OH})^{2+} + \text{H}_2\text{O} =$ $\underline{\text{Co}(\text{NH}_3)_4(\text{OH})_2}^+ + \text{H}^+$ cis	<sup>3</sup> -8.0	-8.0	<sup>4</sup> -8.2	N	521.0	46, 47, 48, 49
trans	<sup>3</sup> -8.1	N	<sup>4</sup> -8.3	N	517.6	47, 49, 50



Table D-13.-Thermodynamic data for cobalt(III) species at 25° C-Continued

Reaction	Log K at ionic strength (M)				$-\Delta_f G^\circ$ of underlined species kJ·mol <sup>-1</sup>	Additional references
	0.0	0.1	1.0	3.0		
$\text{Co}(\text{NH}_3)_5^{3+} + \text{H}_2\text{O} = \underline{\text{Co}(\text{NH}_3)_5(\text{OH})^{2+}} + \text{H}^+$	<sup>3</sup> -6.0	-6.2	-6.5	N	380.0	50, 51
$\text{Co}^{3+} + n\text{CN}^- = \underline{\text{Co}(\text{CN})_n^{3-n}}$ , n = 5	<sup>5</sup> 62.	N	62.	N	-633.7	52
	<sup>6</sup> 73.	N	73.	N	-743.3	53
$\text{Co}(\text{CN})_5^{2-} + \text{H}_2\text{O} = \underline{\text{Co}(\text{CN})_5(\text{OH})^{3-}} + \text{H}^+$	<sup>7</sup> -10.	N	-10.	N	-453.6	54, 55, 56
$\underline{\text{Co}_5(\text{CN})_{12}(\text{s})} = 3\text{Co}^{2+} + 2\text{Co}(\text{CN})_6^{3-}$	<sup>8</sup> -20	N	N	N	-1 205.0	

N No data.

<sup>1</sup>Estimated from data for corresponding complexes of other trivalent metal ions.

<sup>2</sup>Estimated assuming near-zero ionic-strength dependence as for analogous complexes of divalent metal ions.

<sup>3</sup>Estimated from ionic-strength dependence for hydrolysis reactions of metal ions with the same charges and similar sizes.

<sup>4</sup>Estimated from data for related complexes in references 48, 49.

<sup>5</sup>Calculated from reduction potential of -0.43 V given in reference 52, and log K for  $\text{Co}(\text{CN})_5^{3-}$ .

<sup>6</sup>Estimated via enthalpies of reaction  $\text{M}(\text{CN})_5^{2-} + \text{CN}^- = \text{M}(\text{CN})_6^{3-}$ , M = Co, Cr, given in reference 53, and log K for this reaction for M = Cr, assuming equal entropy changes.

<sup>7</sup>Estimated.

<sup>8</sup>Estimated from data for divalent metal hexacyanoferrates(III).



Table D-14.--Thermodynamic data for iron(II) species at 25° C

Reaction	Log K at ionic strength (M)				-Δ <sub>f</sub> G° of underlined species kJ·mol <sup>-1</sup>	Additional references
	0.0	0.1	1.0	3.0		
$\text{Fe}^{2+} + n\text{OH}^- = \underline{\text{Fe}(\text{OH})_n}^{2-n}, n = 1$	4.7	4.2	4.3	N	275.4	
2	7.4	N	N	N	448.1	
3	9.3	N	N	N	616.3	
4	8.9	N	N	N	771.3	
$\underline{\text{Fe}_{0.95}\text{O}(\text{s})} + 0.05\text{Fe}(\text{s}) + \text{H}_2\text{O} =$						
$\text{Fe}^{2+} + 2\text{OH}^-$	-13.6	N	N	N	245.	
$\underline{\text{Fe}(\text{OH})_2(\text{cr})} = \text{Fe}^{2+} + 2\text{OH}^-$	-15.2	N	N	N	492.7	
$\underline{\text{Fe}(\text{OH})_2(\text{am})} = \text{Fe}^{2+} + 2\text{OH}^-$	-14.4	N	N	N	488.1	
$\text{Fe}^{2+} + n\text{Cl}^- = \underline{\text{FeCl}_n}^{2-n}, n = 1$	<sup>1</sup> 1.2	N	-.1	N	223.6	
$\underline{\text{FeS}(\text{s})} + 2\text{H}^+ = \text{Fe}^{2+} + \text{H}_2\text{S}$	3.3	N	N	N	100.	
$\text{Fe}^{2+} + n\text{SO}_4^{2-} = \underline{\text{Fe}(\text{SO}_4)_n}^{2-2n}, n = 1$	<sup>1</sup> 2.3	N	N	N	848.9	
$\text{Fe}^{2+} + n\text{NH}_3 = \underline{\text{Fe}(\text{NH}_3)_n}^{2+}, n = 1$	<sup>1</sup> 1.4	N	N	N	125.8	
2	<sup>1</sup> 2.2	N	N	N	156.9	
3	<sup>1</sup> 2.5	N	N	N	185.1	
4	<sup>1</sup> 2.5	N	N	N	211.6	
$\text{Fe}^{2+} + \text{HCO}_3^- = \underline{\text{Fe}(\text{HCO}_3)}^+$	<sup>1</sup> 1.7	N	N	N	687.9	
$\text{Fe}^{2+} + n\text{CO}_3^{2-} = \underline{\text{Fe}(\text{CO}_3)_n}^{2-2n}, n = 1$	<sup>1</sup> 3.7	N	N	N	640.4	
$n = 2$	<sup>1</sup> 5.7	N	N	N	1,179.8	
$\underline{\text{FeCO}_3(\text{s})} = \text{Fe}^{2+} + \text{CO}_3^{2-}$	-10.2	N	9.7	N	677.5	
$\text{Fe}^{2+} + n\text{NCS}^- = \underline{\text{Fe}(\text{NCS})_n}^{2-n}, n = 1$	1.3	N	N	0.8	6.0	



Table D-14.--Thermodynamic data for iron(II) species at 25° C--Continued

Reaction	Log K at ionic strength (M)				$-\Delta_f G^\circ$ of underlined species kJ·mol <sup>-1</sup>	Additional references
	0.0	0.1	1.0	3.0		
$\text{Fe}^{2+} + n\text{CN}^- = \underline{\text{Fe}(\text{CN})_n}^{2-n}$ , $n = 5$ 6	<sup>2</sup> 27.4 35.4	N N	N N	N N	-614.3 -741.0	59, 60
$\underline{\text{Fe}(\text{CN})_2(\text{s})} = \text{Fe}^{2+} + 2\text{CN}^-$	<sup>3</sup> -17.1	N	N	N	-155.9	
$\underline{\text{HFe}(\text{CN})_5}^{2-} = \text{Fe}(\text{CN})_5^{3-} + \text{H}^+$	<sup>4</sup> -2.7	-2.7	N	N	-598.9	61, 62
$\text{Fe}(\text{CN})_5^{3-} + \text{H}_2\text{O} = \underline{\text{Fe}(\text{CN})_5(\text{OH})}^{4-} + \text{H}^+$	<-14.	N	N	N	N	59, 63
$\underline{\text{HFe}(\text{CN})_6}^{3-} = \text{Fe}(\text{CN})_6^{4-} + \text{H}^+$	-4.2	-3.2	N	-2.8	-717.1	64
$\underline{\text{H}_2\text{Fe}(\text{CN})_6}^{2-} = \text{HFe}(\text{CN})_6^{3-} + \text{H}^+$	-2.6	-1.2	N	-1.8	-702.2	64

N No data.

<sup>1</sup>Estimated from data for corresponding complexes of other divalent metal ions.<sup>2</sup>Estimated. Data given for  $\text{Fe}(\text{CN})_5^{3-} + \text{CN}^- = \text{Fe}(\text{CN})_6^{4-}$  in references 59, 60 at ionic strength 1.0M.<sup>3</sup>Derived from log K = -16 for  $\text{Fe}_2\text{Fe}(\text{CN})_6(\text{s}) = 2\text{Fe}^{2+} + \text{Fe}(\text{CN})_6^{4-}$  estimated from data for other divalent metal hexacyanoferrates(II).<sup>4</sup>Estimated.



Table D-15.--Thermodynamic data for iron(III) species at 25° C

Reaction	Log K at ionic strength (M)				$-\Delta_f G^\circ$ of underlined species kJ·mol <sup>-1</sup>	Additional references
	0.0	0.1	1.0	3.0		
$\text{Fe}^{3+} + n\text{OH}^- = \underline{\text{Fe}(\text{OH})_n}^{3-n}$ , n = 1	11.8	11.3	11.1	11.2	241.7	57
2	22.3	N	22.0	22.1	458.9	57
3	<sup>1</sup> 30.3	N	N	N	661.9	57
4	34.4	N	N	N	842.6	57
$2\text{Fe}^{3+} + 2\text{OH}^- = \underline{\text{Fe}_2(\text{OH})_2}^{4+}$	25.1	24.7	25.0	25.4	491.9	57
$3\text{Fe}^{3+} + 4\text{OH}^- = \underline{\text{Fe}_3(\text{OH})_4}^{5+}$	49.7	N	46.4	51.0	963.9	57
$\underline{\text{Fe}_2\text{O}_3(\text{s})} + 3\text{H}_2\text{O} = 2\text{Fe}^{3+} + 6\text{OH}^-$	-83.4	N	N	N	742.	57
$\underline{\text{FeO}(\text{OH})}(\text{goe}) + \text{H}_2\text{O} = \text{Fe}^{3+} + 3\text{OH}^-$	-41.7	N	N	N	490.	57
$\underline{\text{Fe}(\text{OH})_3}(\text{aged}) = \text{Fe}^{3+} + 3\text{OH}^-$	-39.	N	N	N	711.5	57
$\underline{\text{Fe}(\text{OH})_3}(\text{fresh}) = \text{Fe}^{3+} + 3\text{OH}^-$	-37.	N	N	N	700.1	57
$\underline{\text{Fe}_3\text{O}_4(\text{s})} + 2\text{H}_2\text{O} = 2\underline{\text{FeO}(\text{OH})}(\text{goe}) + \underline{\text{Fe}^{2+}} + 2\text{OH}^-$	-18.1	N	N	N	1,015.	
$\text{Fe}^{3+} + n\text{Cl}^- = \underline{\text{FeCl}_n}^{3-n}$ , n = 1	1.5	N	.6	.8	156.8	
2	2.1	N	.7	N	291.4	
$\underline{\text{FeS}(\text{s})} + \underline{\text{FeS}_2(\text{s})} + 6\text{H}^+ = 2\text{Fe}^{3+} + 3\text{H}_2\text{S}$	-25.0	N	N	N	260.	
$\text{Fe}^{3+} + n\text{SO}_4^{2-} = \underline{\text{Fe}(\text{SO}_4)_n}^{3-2n}$ , n = 1	4.0	N	2.0	1.9	784.3	
2	5.4	N	N	2.1	1,536.8	
$\text{Fe}^{3+} + n\text{NCS}^- = \underline{\text{Fe}(\text{NCS})_n}^{3-n}$ , n = 1	3.0	2.4	2.1	2.2	-58.6	
2	3.6	3.6	3.3	3.7	-147.9	
$\text{Fe}^{3+} + n\text{CN}^- = \underline{\text{Fe}(\text{CN})_n}^{3-n}$ , n = 5	<sup>2</sup> 34.8	N	N	N	-646.4	59, 65, 66
6	<sup>3</sup> 42.3	N	N	N	-776.0	



Table D-15.--Thermodynamic data for iron(III) species at 25° C--Continued

Reaction	Log K at ionic strength (M)				$-\Delta_f G^\circ$ of underlined species kJ·mol <sup>-1</sup>	Additional references
	0.0	0.1	1.0	3.0		
$\text{Fe}(\text{CN})_5^{2-} + \text{H}_2\text{O} = \underline{\text{Fe}(\text{CN})_5(\text{OH})^{3-}} + \text{H}^+$	<sup>4</sup> -8.	N	-8.4	N	-454.8	59
$\text{Fe}^{3+} + \text{Fe}(\text{CN})_6^{3-} = \underline{\text{Fe}_2(\text{CN})_6}$	<sup>4</sup> 3.	2.3	1.4	N	-741.9	67
$\underline{\text{Fe}_5(\text{CN})_{12}} = 3\text{Fe}^{2+} + 2\text{Fe}(\text{CN})_6^{3-}$	<sup>4</sup> -40.	N	N	N	-1,049.8	
$\underline{\text{Fe}_7(\text{CN})_{18}} = 4\text{Fe}^{3+} + 3\text{Fe}(\text{CN})_6^{4-}$	-84.	N	N	N	-1,675.5	68

N No data.

<sup>1</sup>Estimated from data for corresponding complexes of other trivalent metal ions.<sup>2</sup>Calculated via estimated reduction potential of +0.33 V from data at ionic strength 1.0M in references 59, 65, 66, via ionic-strength dependence of reduction potential of  $\text{Fe}(\text{CN})_6^{3-}$  (reference 10).<sup>3</sup>Calculated from standard reduction potential of +0.36 V and log K for  $\text{Fe}(\text{CN})_6^{4-}$ .<sup>4</sup>Estimated.



Table D-16.-Thermodynamic data for manganese(II) species at 25° C

Reaction	Log K at ionic strength (M)				-Δ <sub>f</sub> G° of underlined species kJ·mol <sup>-1</sup>	Additional references
	0.0	0.1	1.0	3.0		
$\text{Mn}^{2+} + n\text{OH}^- = \underline{\text{Mn}(\text{OH})_n}^{2-n}, n = 1$	3.4	2.9	3.0	N	407.7	
2	<sup>1</sup> 6.	N	N	N	579.8	
3	<sup>1</sup> 8.	N	N	N	748.6	
4	8.	N	N	N	905.9	
$\underline{\text{MnO}}(\text{s}) + \text{H}_2\text{O} = \text{Mn}^{2+} + 2\text{OH}^-$	-9.6				363.	
$\underline{\text{Mn}(\text{OH})_2}(\text{cr}) = \text{Mn}^{2+} + 2\text{OH}^-$	-12.8	N	N	N	618.7	
$\underline{\text{Mn}(\text{OH})_2}(\text{am}) = \text{Mn}^{2+} + 2\text{OH}^-$	-12.8	N	N	N	618.7	
$\text{Mn}^{2+} + n\text{Cl}^- = \underline{\text{MnCl}_n}^{2-n}, n = 1$	<sup>1</sup> .1	N	-.2	N	362.8	
$\underline{\text{MnS}}(\text{s}) + 2\text{H}^+ = \text{Mn}^{2+} + \text{H}_2\text{S}$	7.0	N	N	N	219.	
$\text{Mn}^{2+} + n\text{SO}_4^{2-} = \underline{\text{Mn}(\text{SO}_4)_n}^{2-2n}, n = 1$	2.3	N	.6	0.6	988.6	
$\text{Mn}^{2+} + n\text{NH}_3 = \underline{\text{Mn}(\text{NH}_3)_n}^{2+}, n = 1$	<sup>2</sup> .9	N	N	N	262.6	
2	<sup>2</sup> 1.3	N	N	N	291.4	
3	<sup>2</sup> 1.3	N	N	N	317.9	
4	<sup>2</sup> .8	N	N	N	341.6	
$\text{Mn}^{2+} + \text{HCO}_3^- = \underline{\text{Mn}(\text{HCO}_3)}^+$	1.3	N	N	.5	825.3	
$\text{Mn}^{2+} + n\text{CO}_3^{2-} = \underline{\text{Mn}(\text{CO}_3)_n}^{2-2n}, n = 1$	<sup>1</sup> 3.5	N	N	N	779.0	71
$\underline{\text{MnCO}_3}(\text{s}) = \text{Mn}^{2+} + \text{CO}_3^{2-}$	-10.6	N	N	N	819.5	70
$\text{Mn}^{2+} + n\text{NCS}^- = \underline{\text{Mn}(\text{NCS})_n}^{2-n}, n = 1$	1.2	N	.6	N	145.2	
$\text{Mn}^{2+} + n\text{CN}^- = \underline{\text{Mn}(\text{CN})_n}^{2-n}, n = 6$	<sup>3</sup> 10.	N	N	N	-746.3	43
$\underline{\text{Mn}(\text{CN})_2}(\text{s}) = \text{Mn}^{2+} + 2\text{CN}^-$	<sup>4</sup> -8.7	N	N	N	-64.1	

N No data.

<sup>1</sup>Estimated from data for corresponding complexes of other divalent metal ions.<sup>2</sup>Estimated from data at 20° C and ionic strength 2.0M with aid of data for corresponding complexes of other divalent metals.<sup>3</sup>Extrapolated from data for lower complexes in reference 43, considering known (reference 10) low stability of this complex. Reported reduction potential of  $\text{Mn}(\text{CN})_6^{3-}$ , -0.24 V, is open to question (reference 10).<sup>4</sup>Estimated from data for divalent metal hexacyanoferrates(II).



Table D-17.--Thermodynamic data for manganese(III) species at 25° C

Reaction	Log K at ionic strength (M)				$-\Delta_f G^\circ$ of underlined species $\text{kJ}\cdot\text{mol}^{-1}$	Additional references
	0.0	0.1	1.0	3.0		
$\text{Mn}^{3+} + n\text{OH}^- = \underline{\text{Mn}(\text{OH})_n^{3-n}}$ , $n = 1$	<sup>1</sup> 13.	N	N	14.6	312.9	
2	<sup>1</sup> 24.	N	N	28.5	533.0	
3	<sup>1</sup> 31.	N	N	N	730.2	
4	<sup>1</sup> 35.	N	N	N	910.4	
$2\text{Mn}^{3+} + 2\text{OH}^- = \underline{\text{Mn}_2(\text{OH})_2^{4+}}$	<sup>1</sup> 31.	N	N	N	654.3	
$\underline{\text{Mn}_2\text{O}_3(\text{s})} + 3\text{H}_2\text{O} = 2\text{Mn}^{3+} + 6\text{OH}^-$	-85.0	N	N	N	881.	
$\underline{\text{MnO}(\text{OH})}(\text{man}) + \text{H}_2\text{O} = \text{Mn}^{3+} + 3\text{OH}^-$	-42.2	N	N	N	557.	71
$\underline{\text{Mn}(\text{OH})_3}(\text{aged}) = \text{Mn}^{3+} + 3\text{OH}^-$	<sup>1</sup> -40.	N	N	N	781.6	
$\underline{\text{Mn}(\text{OH})_3}(\text{fresh}) = \text{Mn}^{3+} + 3\text{OH}^-$	<sup>1</sup> -38.	N	N	N	770.2	
$\underline{\text{Mn}_3\text{O}_4(\text{s})} + 2\text{H}_2\text{O} = 2\text{MnO}(\text{OH}) (\text{man}) + \text{Mn}^{2+} + 2\text{OH}^-$	-17.1	N	N	N	1,283.	
$2\text{MnO}(\text{OH}) (\text{man}) = \underline{\text{MnO}_2(\text{pyr})} + \text{Mn}^{2+} + 2\text{OH}^-$	-18.1	N	N	N	465.	
$2\text{MnO}(\text{OH}) (\text{man}) = \underline{\text{MnO}_2(\text{ppt})} + \text{Mn}^{2+} + 2\text{OH}^-$	-19.8	N	N	N	455.3	71
$\text{Mn}^{3+} + n\text{Cl}^- = \underline{\text{MnCl}_n^{3-n}}$ , $n = 1$	<sup>1</sup> 1.8	N	N	1.1	222.9	
2	<sup>1</sup> 2.5	N	N	N	358.1	
$\underline{\text{MnS}(\text{s})} + \underline{\text{MnS}_2(\text{s})} + 6\text{H}^+ = 2\text{Mn}^{3+} + 3\text{H}_2\text{S}$	34.7	N	N	N	444.	
$\text{Mn}^{3+} + n\text{SO}_4^{2-} = \underline{\text{Mn}(\text{SO}_4)_n^{3-2n}}$ , $n = 1$	<sup>1</sup> 4.0	N	N	N	848.7	
2	<sup>1</sup> 5.4	N	N	N	1,601.2	
$\text{Mn}^{3+} + n\text{CN}^- = \underline{\text{Mn}(\text{CN})_n^{3-n}}$ , $n = 5$	<sup>2</sup> 34.	N	N	N	-586.5	
6	<sup>3</sup> 35.	N	N	N	-753.2	72



Table D-17.-Thermodynamic data for manganese(III) species at 25° C-Continued

Reaction	Log K at ionic strength (M)				$-\Delta_f G^\circ$ of underlined species $\text{kJ}\cdot\text{mol}^{-1}$	Additional references
	0.0	0.1	1.0	3.0		
$\text{Mn}(\text{CN})_5^{2-} + \text{H}_2\text{O} = \underline{\text{Mn}(\text{CN})_5(\text{OH})^{3-}} + \text{H}^+$	<sup>1</sup> -9.	N	N	N	-400.7	
$\underline{\text{Mn}_2(\text{CN})_6(\text{s})} = 2\text{Mn}^{3+} + 6\text{CN}^-$	<sup>4</sup> -43.	N	N	N	-626.2	
$\underline{\text{Mn}_5(\text{CN})_{12}(\text{s})} = 3\text{Mn}^{2+} + 2\text{Mn}(\text{CN})_6^{3-}$	<sup>5</sup> -20.	N	N	N	-699.2	
$2\text{Mn}(\text{CN})_6^{3-} + 6\text{H}^+ = \underline{\text{Mn}(\text{CN})_6^{2-}} + \text{Mn}^{2+} + 6\text{HCN}$	>0.	N	N	N	<sup>6</sup> -900.	73, 74

N No data.

<sup>1</sup>Estimated from data for corresponding complexes of other trivalent metal ions.<sup>2</sup>Estimated, based on observed synthesis of solid derivatives (reference 10).<sup>3</sup>Estimated as in reference 10 with log K = -40 for solubility of  $\text{Mn}(\text{OH})_3$  precipitate.<sup>4</sup>Estimated from observed insolubility (reference 73) via log K = -8 for  $\text{Mn}_2(\text{CN})_6 = \text{Mn}^{3+} + \text{Mn}(\text{CN})_6^{3-}$ .<sup>5</sup>Estimated from data for divalent metal hexacyanoferrates(III).<sup>6</sup>Rough estimate from occurrence of stated reaction and observed decomposition of  $\text{K}_2\text{Mn}(\text{CN})_6$  in water (reference 10).



Table D-18.--Thermodynamic data for chromium(III) species at 25° C

Reaction	Log K at ionic strength (M)				-Δ <sub>f</sub> G° of underlined species kJ·mol <sup>-1</sup>	Additional references
	0.0	0.1	1.0	3.0		
$\text{Cr}^{3+} + n\text{OH}^- = \underline{\text{Cr}(\text{OH})_n}^{3-n}$ , n = 1	10.0	9.8	9.5	N	440.4	77
2	<sup>1</sup> 18.	17.3	21.5	N	643.3	77
3	<sup>1</sup> 25.	N	N	N	840.6	
4	<sup>1</sup> 30.	N	N	N	1,026.4	
$2\text{Cr}^{3+} + 2\text{OH}^- = \underline{\text{Cr}_2(\text{OH})_2}^{4+}$	<sup>1</sup> 22.6	N	22.4	N	895.6	77
$3\text{Cr}^{3+} + 4\text{OH}^- = \underline{\text{Cr}_3(\text{OH})_4}^{5+}$	<sup>1</sup> 47	N	46.4	N	1,575.5	77
$\underline{\text{Cr}_2\text{O}_3(\text{s})} + 3\text{H}_2\text{O} = 2\text{Cr}^{3+} + 6\text{OH}^-$	-65.6	N	N	N	1,059.	
$\underline{\text{CrO}(\text{OH})(\text{s})} + \text{H}_2\text{O} = \text{Cr}^{3+} + 3\text{OH}^-$	<sup>1</sup> -34.	N	N	N	654.8	
$\underline{\text{Cr}(\text{OH})_3(\text{aged})} = \text{Cr}^{3+} + 3\text{OH}^-$	<sup>1</sup> -32.	N	N	N	880.6	
$\underline{\text{Cr}(\text{OH})_3(\text{fresh})} = \text{Cr}^{3+} + 3\text{OH}^-$	-30.	N	N	N	869.1	
$\text{Cr}^{3+} + n\text{Cl}^- = \underline{\text{CrCl}_n}^{3-n}$ , n = 1	<sup>1</sup> .5	N	-.5	-0.2	360.1	
2	<sup>1</sup> .6	N	N	N	491.8	
$\underline{\text{Cr}_2\text{S}_3(\text{s})} + 6\text{H}^+ = 2\text{Cr}^{3+} + 3\text{H}_2\text{S}$	33.7	N	N	N	343.	
$\text{Cr}^{3+} + n\text{SO}_4^{2-} = \underline{\text{Cr}(\text{SO}_4)_n}^{3-2n}$ , n = 1	<sup>1</sup> 4.0	N	N	N	993.3	
2	<sup>1</sup> 5.4	N	N	N	1,745.8	
$\text{Cr}^{3+} + n\text{NH}_3 = \underline{\text{Cr}(\text{NH}_3)_n}^{3+}$ , n = 3fac	<sup>2</sup> 7.8	N	N	N	350.0	
3mer	<sup>2</sup> 7.2	N	N	N	346.6	
4cis	<sup>3</sup> 9.5	N	N	N	386.2	
4tr	<sup>3</sup> 8.6	N	N	N	381.1	
5	<sup>3</sup> 10.8	N	N	N	420.1	
6	<sup>3</sup> 12.	N	N	N	453.5	
$\text{Cr}(\text{NH}_3)_3^{3+} + \text{H}_2\text{O} = \underline{\text{Cr}(\text{NH}_3)_3(\text{OH})}^{2+}$						
+ H <sup>+</sup> fac	<sup>4</sup> -4.5	N	-5.0	N	561.5	78
mer	<sup>4</sup> -4.0	N	-4.5	N	561.0	78



Table D-18.--Thermodynamic data for chromium(III) species at 25° C--Continued

Reaction	Log K at ionic strength (M)				$-\Delta_f G^\circ$ of underlined species kJ·mol <sup>-1</sup>	Additional references
	0.0	0.1	1.0	3.0		
$\text{Cr}(\text{NH}_3)_3(\text{OH})^{2+} + \text{H}_2\text{O} =$						
$\text{Cr}(\text{NH}_3)_3(\text{OH})_2^+ + \text{H}^+$ fac	<sup>4</sup> -7.1	N	-7.3	N	758.2	78
mer	<sup>4</sup> -6.9	N	-7.1	N	758.8	78
$\text{Cr}(\text{NH}_3)_3(\text{OH})_2^+ + \text{H}_2\text{O} =$						
$\text{Cr}(\text{NH}_3)_3(\text{OH})_3 + \text{H}^+$ fac	<sup>4</sup> -9.3	N	-9.3	N	942.3	78
mer	<sup>4</sup> -9.2	N	-9.2	N	943.5	78
$\text{Cr}(\text{NH}_3)_4^{3+} + \text{H}_2\text{O} = \text{Cr}(\text{NH}_3)_4(\text{OH})^{2+}$						
+ H <sup>+</sup> cis	<sup>4</sup> -4.5	N	-5.0	N	597.7	78
trans	<sup>4</sup> -3.9	N	-4.4	N	596.0	78
$\text{Cr}(\text{NH}_3)_4(\text{OH})^{2+} + \text{H}_2\text{O} =$						
$\text{Cr}(\text{NH}_3)_4(\text{OH})_2^{1+} + \text{H}^+$ cis	<sup>4</sup> -7.3	N	-7.5	N	793.3	78
trans	<sup>4</sup> -7.6	N	-7.8	N	789.8	78
$\text{Cr}(\text{NH}_3)_5^{3+} + \text{H}_2\text{O} = \text{Cr}(\text{NH}_3)_5(\text{OH})^{2+} + \text{H}^+$	<sup>4</sup> -4.7	-5.1	-5.2	N	630.5	50, 78
$\text{Cr}^{3+} + n\text{NCS}^- = \text{Cr}(\text{NCS})_n^{3-n}, n = 1$	3.1	N	N	N	151.0	
2	<sup>1</sup> 3.6	N	N	N	61.1	
$\text{Cr}^{3+} + n\text{CN}^- = \text{Cr}(\text{CN})_n^{3-n}, n = 5$	<sup>5</sup> 28.	N	29.1	N	-476.2	
6	<sup>5</sup> 33.	N	34.	N	-620.0	53
$\text{Cr}(\text{CN})_5^{2-} + \text{H}_2\text{O} = \text{Cr}(\text{CN})_5(\text{OH})^{3-} + \text{H}^+$	<sup>5</sup> -9.	-8.8	-9.0	N	-290.3	79

N No data.

<sup>1</sup>Estimated from data for corresponding complexes of other trivalent metal ions.<sup>2</sup>Estimated from data for tetrammine and pentammine complexes and trends in formation log K values for other metal ammine complexes.<sup>3</sup>Estimated from data at ionic strength 4.5 M assuming near-zero ionic strength dependence; compare data for NH<sub>3</sub> complexes of divalent metal ions.<sup>4</sup>Estimated from ionic-strength dependence of hydrolysis reactions of metal ions having the same charges and similar sizes.<sup>5</sup>Estimated.



Table D-19.-Thermodynamic data for thallium(I) species at 25° C

Reaction	Log K at ionic strength (M)				-Δ <sub>f</sub> G° of underlined species kJ·mol <sup>-1</sup>	Additional references
	0.0	0.1	1.0	3.0		
$\text{Tl}^+ + n\text{OH}^- = \underline{\text{Tl}(\text{OH})_n}^{1-n}, n = 1$	0.8	N	0.3	0.1	193.5	80
$\text{Tl}^+ + n\text{Cl}^- = \underline{\text{TlCl}}_n^{1-n}, n = 1$	.5	N	.0	-.1	165.7	
$\text{TlCl} = \text{Tl}^+ + \text{Cl}^-$	.0	N	-.1	-1.0	294.0	
$\underline{\text{TlCl}} = \text{Tl}^+ + \text{Cl}^-$	-3.8	N	-3.2	-3.1	184.9	
$\underline{\text{Tl}_2\text{S}(\text{s})} + 2\text{H}^+ = 2\text{Tl}^+ + \text{H}_2\text{S}$	-.4	N	-.7	N	93.	
$\text{Tl}^+ + n\text{SH}^- = \underline{\text{Tl}(\text{SH})_n}^{1-n}, n = 1$	<sup>1</sup> 5.3	N	2.3	N	49.6	
$2\text{Tl}^+ + n\text{SH}^- = \underline{\text{Tl}_2(\text{SH})_n}^{2-n}, n = 1$	<sup>1</sup> 6.6	N	5.8	N	88.6	
$2\text{Tl}^+ + 2\text{SH}^- + 2\text{OH}^- = \underline{\text{Tl}_2\text{O}(\text{SH})_2}^{2-} + \text{H}_2\text{O}$	<sup>1</sup> 18.0	N	16.7	N	276.6	
$2\text{Tl}^+ + 3\text{SH}^- + \text{OH}^- = \underline{\text{Tl}_2\text{S}(\text{SH})_2}^{2-} + \text{H}_2\text{O}$	<sup>1</sup> 16.3	N	15.0	N	455.9	
$\text{Tl}^+ + n\text{S}_2\text{O}_3^{2-} = \underline{\text{Tl}(\text{S}_2\text{O}_3)_n}^{1-2n}, n = 1$	<sup>1</sup> 2.3	N	1.6	N	567.2	
	<sup>1</sup> 2.8	N	1.9	N	1,092.6	
$\text{Tl}^+ + \text{SO}_4^{2-} = \underline{\text{Tl}(\text{SO}_4)}^{1-}$	1.4	N	.4	-.1	784.1	
$\text{Tl}^+ + n\text{NCS}^- = \underline{\text{Tl}(\text{NCS})_n}^{1-n}, n = 1$	.6	N	.2	.1	-57.7	
	<sup>1</sup> 0.0	N	0.0	-.1	-153.8	
$\underline{\text{TlNCS}} = \text{Tl}^+ + \text{NCS}^-$	-3.8	N	N	-3.2	-39.4	

N No data.

<sup>1</sup>Estimated from ionic-strength dependence of log K for corresponding Cu and Ag complexes.



Table D-20.--Thermodynamic data for thallium(III) species at 25° C

Reaction	Log K at ionic strength (M)				$-\Delta_f G^\circ$ of underlined species kJ·mol <sup>-1</sup>	Additional references
	0.0	0.1	1.0	3.0		
$\text{Tl}^{3+} + n\text{OH}^- = \underline{\text{Tl}(\text{OH})_n}^{3-n}$ , n = 1	13.4	12.8	12.7	13.1	18.8	
2	26.6	25.2	25.4	25.8	251.4	
3	38.7	37.5	N	N	477.8	
4	41.0	N	N	39.4	648.2	
$\underline{\text{Tl}_2\text{O}_3(\text{s})} + 3\text{H}_2\text{O} = 2\text{Tl}^{3+} + 6\text{OH}^-$	-89.4	N	N	-90.0	312.	
$\text{Tl}^{3+} + n\text{Cl}^- = \underline{\text{TlCl}_n}^{3-n}$ , n = 1	7.7	N	N	7.1	-39.8	
2	13.5	N	N	12.5	124.5	
3	16.5	N	N	15.8	272.8	
4	18.3	N	N	18.0	414.3	
$\text{TlCl}^{2+} + \text{H}_2\text{O} = \underline{\text{TlCl}(\text{OH})}^{2+} + \text{H}^+$	<sup>1</sup> 2.	N	N	1.9	185.9	
$\text{Tl}^{3+} + n\text{SO}_4^{2-} = \underline{\text{Tl}(\text{SO}_4)_n}^{3-2n}$ , n = 1	<sup>2</sup> 4.7	N	N	2.3	556.3	
2	<sup>2</sup> 6.3	N	N	N	1,310.0	
$\text{Tl}^{3+} + n\text{CN}^- = \underline{\text{Tl}(\text{CN})_n}^{3-n}$ , n = 1	<sup>3</sup> 13.	N	N	<sup>4</sup> 13.2	-313.2	81
2	<sup>3</sup> 26.	N	N	<sup>4</sup> 26.5	-411.4	81
3	<sup>3</sup> 34.	N	N	<sup>4</sup> 35.2	-538.1	81
4	<sup>3</sup> 40.	N	N	<sup>4</sup> 42.6	-676.3	81

N No data.

<sup>1</sup>Estimated by comparison with data for analogous Hg(II) complexes.<sup>2</sup>Estimated from data for corresponding rare earth, Fe, and In complexes.<sup>3</sup>Estimated assuming same ionic-strength dependence as for corresponding halide complexes.<sup>4</sup>Ionic strength 4.0M.



Table D-21.--Thermodynamic data for lead(II) species at 25° C

Reaction	Log K at ionic strength (M)				$-\Delta_f G^\circ$ of underlined species kJ·mol <sup>-1</sup>	Additional references
	0.0	0.1	1.0	3.0		
$\text{Pb}^{2+} + n\text{OH}^- = \underline{\text{Pb}(\text{OH})_n}^{2-n}$ , $n = 1$	6.4	6.0	N	6.3	217.8	
2	10.9	N	N	10.9	400.8	
3	13.9	N	N	13.7	575.2	
$2\text{Pb}^{2+} + \text{OH}^- = \underline{\text{Pb}_2(\text{OH})}^{3+}$	7.6	N	N	7.8	248.7	
$3\text{Pb}^{2+} + 4\text{OH}^- = \underline{\text{Pb}_3(\text{OH})_4}^{2+}$	32.1	N	N	34.0	884.4	
$4\text{Pb}^{2+} + 4\text{OH}^- = \underline{\text{Pb}_4(\text{OH})_4}^{4+}$	36.0	N	N	37.5	930.7	
$6\text{Pb}^{2+} + 8\text{OH}^- = \underline{\text{Pb}_6(\text{OH})_8}^{4+}$	68.4	N	N	71.3	1,792.8	
$\underline{\text{PbO}(\text{tetr})} + \text{H}_2\text{O} = \text{Pb}^{2+} + 2\text{OH}^-$	-15.3	N	N	N	188.9	
$\underline{\text{PbO}(\text{orhb})} + \text{H}_2\text{O} = \text{Pb}^{2+} + 2\text{OH}^-$	-15.2	N	N	N	187.9	
$\underline{\text{Pb}(\text{OH})_2(\text{am})} = \text{Pb}^{2+} + 2\text{OH}^-$	-14.9	N	N	N	423.6	
$\text{Pb}^{2+} + n\text{Cl}^- = \underline{\text{PbCl}_n}^{2-n}$ , $n = 1$	1.6	N	0.9	1.1	164.3	
2	2.2	N	1.2	1.6	299.0	
3	1.8	N	1.1	1.9	427.9	
4	1.1	N	N	1.0	555.1	
$\underline{\text{PbCl}_2(\text{s})} = \text{Pb}^{2+} + 2\text{Cl}^-$	-4.8	N	N	-5.0	314.1	
$\underline{\text{Pb}(\text{OH})\text{Cl}(\text{s})} = \text{Pb}^{2+} + \text{OH}^- + \text{Cl}^-$	-13.4	N	N	N	389.0	82
$\underline{\text{Pb}_2(\text{OH})_3\text{Cl}(\text{s})} = 2\text{Pb}^{2+} + 3\text{OH}^- + \text{Cl}^-$	-16.9	N	N	N	747.6	83
$\underline{\text{PbS}(\text{s})} + 2\text{H}^+ = \text{Pb}^{2+} + \text{H}_2\text{S}$	-7.9	N	N	N	97.	
$\text{Pb}^{2+} + n\text{S}_2\text{O}_3^{2-} = \underline{\text{Pb}(\text{S}_2\text{O}_3)_n}^{2-2n}$ , $n = 1$	3.6	N	N	2.4	567.0	
2	6.5	N	N	4.9	1,106.1	
$\underline{\text{Pb}(\text{S}_2\text{O}_3)(\text{s})} = \text{Pb}^{2+} + \text{S}_2\text{O}_3^{2-}$	-8.3	N	N	N	594.5	
$\text{Pb}^{2+} + n\text{SO}_4^{2-} = \underline{\text{Pb}(\text{SO}_4)_n}^{2-2n}$ , $n = 1$	2.7	2.1	N	N	783.9	
$\underline{\text{PbSO}_4(\text{s})} = \text{Pb}^{2+} + \text{SO}_4^{2-}$	7.8	7.0	6.2	N	813.0	84



Table D-21.--Thermodynamic data for lead(II) species at 25° C--Continued

Reaction	Log K at ionic strength (M)				$-\Delta_f G^\circ$ of underlined species kJ·mol <sup>-1</sup>	Additional references
	0.0	0.1	1.0	3.0		
$\frac{\text{Pb}_2\text{O}(\text{SO}_4)(\text{s})}{2\text{OH}^- + \text{SO}_4^{2-}} + \text{H}_2\text{O} = 2\text{Pb}^{2+}$	-27.0	N	N	N	1,024.	84
$\frac{\text{Pb}_3\text{O}_2(\text{SO}_4)(\text{s})}{+ 4\text{OH}^- + \text{SO}_4^{2-}} + 2\text{H}_2\text{O} = 3\text{Pb}^{2+}$	-41.8	N	N	N	1,210.	84
$\frac{\text{Pb}_5\text{O}_4(\text{SO}_4)(\text{s})}{+ 8\text{OH}^- + \text{SO}_4^{2-}} + 4\text{H}_2\text{O} = 5\text{Pb}^{2+}$	-75.5	N	N	N	1,605.	84
$\text{Pb}^{2+} + \text{HCO}_3^- = \underline{\text{Pb}(\text{HCO}_3)^+}$	<sup>1</sup> 3.	N	N	N	628.0	
$\text{Pb}^{2+} + n\text{CO}_3^{2-} = \underline{\text{Pb}(\text{CO}_3)_n}^{2-2n}, \quad n = 1$ $n = 2$	<sup>2</sup> 6.	N	N	N	586.2	
	<sup>2</sup> 9.	N	N	N	1,131.4	
$\underline{\text{PbCO}_3(\text{s})} = \text{Pb}^{2+} + \text{CO}_3^{2-}$	-12.0	N	N	-11.2	674.1	
$\frac{\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2(\text{s})}{3\text{Pb}^{2+} + 2\text{OH}^- + 2\text{CO}_3^{2-}} =$	-47.	-46.	N	N	1,710.9	85
$\frac{\text{Pb}_{10}\text{O}(\text{OH})_6(\text{CO}_3)_6(\text{s})}{10\text{Pb}^{2+} + 8\text{OH}^- + 6\text{CO}_3^{2-}} + \text{H}_2\text{O} =$	-120.8	N	N	N	5,118.7	84
$\text{Pb}^{2+} + n\text{NCS}^- = \underline{\text{Pb}(\text{NCS})_n}^{2-n}, \quad n = 1$ $n = 2$ $n = 3$	1.2	N	N	.8	-61.9	
	1.5	N	N	1.0	-152.8	
	1.2	N	N	1.0	-247.3	

N No data.

<sup>1</sup>Estimated from data for corresponding complexes of other divalent metal ions.<sup>2</sup>Estimated from data at ionic strength 0.3M and data for corresponding complexes of other divalent metal ions.



Table D-22.--Thermodynamic data for magnesium(II) species at 25° C

Reaction	Log K at ionic strength (M)				$-\Delta_f G^\circ$ of underlined species kJ·mol <sup>-1</sup>	Additional references
	0.0	0.1	1.0	3.0		
$Mg^{2+} + nOH^- = \underline{Mg(OH)_n}^{2-n}$ , $n = 1$	2.8	N	N	2.2	629.3	
$\underline{Mg(OH)_2}(\text{cr}) = Mg^{2+} + 2OH^-$	-11.1	N	N	-11.1	834.0	
$\underline{Mg(OH)_2}(\text{am}) = Mg^{2+} + 2OH^-$	-9.3	N	N	N	823.7	
$Mg^{2+} + nSO_4^{2-} = \underline{Mg(SO_4)_n}^{2-2n}$ , $n = 1$	2.2	1.5	0.8	N	1,213.1	
$\underline{MgCO_3}(\text{s}) = Mg^{2+} + CO_3^{2-}$	-7.5	N	N	N	1,026.8	
$\underline{MgCO_3 \cdot 3H_2O}(\text{s}) = Mg^{2+} + CO_3^{2-} + 3H_2O$	-4.7	N	N	N	1,722.4	
$\underline{MgCO_3 \cdot 5H_2O}(\text{s}) = Mg^{2+} + CO_3^{2-} + 5H_2O$	-4.5	N	N	N	2,195.7	
$Mg^{2+} + CO_3^{2-} = \underline{Mg(CO_3)}$	2.9	N	N	1.7	1,000.6	
$Mg^{2+} + HCO_3^- = \underline{Mg(HCO_3)}^+$	1.0	N	N	0.1	1,048.6	

N No data.



Table D-23.-Thermodynamic data for calcium(II) species at 25° C

Reaction	Log K at ionic strength (M)				$-\Delta_f G^\circ$ of underlined species $\text{kJ}\cdot\text{mol}^{-1}$	Additional references
	0.0	0.1	1.0	3.0		
$\text{Ca}^{2+} + n\text{OH}^- = \underline{\text{Ca}(\text{OH})_n}^{2-n}, n = 1$	1.3	1.0	N	0.7	717.8	
$\underline{\text{Ca}(\text{OH})_2(\text{cr})} = \text{Ca}^{2+} + 2\text{OH}^-$	-5.2	N	N	N	897.4	
$\underline{\text{CaSO}_4(\text{s})} = \text{Ca}^{2+} + \text{SO}_4^{2-}$	-4.4	N	N	N	1,321.7	
$\underline{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}(\text{s})} = \text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O}$	-4.6	N	2.9	3.2	1,798.3	
$\text{Ca}^{2+} + n\text{SO}_4^{2-} = \underline{\text{Ca}(\text{SO}_4)_n}^{2-2n}, n = 1$	2.3	1.5	1.0	N	1,310.7	
$\underline{\text{CaCO}_3(\text{s, cal})} = \text{Ca}^{2+} + \text{CO}_3^{2-}$	-8.5	N	N	N	1,129.6	
$\underline{\text{CaCO}_3(\text{s, ara})} = \text{Ca}^{2+} + \text{CO}_3^{2-}$	-8.3	N	N	N	1,128.5	
$\underline{\text{CaCO}_3(\text{s, vat})} = \text{Ca}^{2+} + \text{CO}_3^{2-}$	-7.9	N	N	N	1,126.2	
$\underline{\text{CaCO}_3 \cdot \text{H}_2\text{O}(\text{s})} = \text{Ca}^{2+} + \text{CO}_3^{2-} + \text{H}_2\text{O}$	-7.6	N	N	N	1,361.7	
$\text{Ca}^{2+} + \text{CO}_3^{2-} = \underline{\text{Ca}(\text{CO}_3)}$	3.2	N	N	N	1,099.4	
$\text{Ca}^{2+} + \text{HCO}_3^- = \underline{\text{Ca}(\text{HCO}_3)^+}$	1.3	N	N	N	1,147.4	

N No data.



Table D-24.--Thermodynamic data for gallium(III)  
and indium(III) species at 25° C

(Values for CN<sup>-</sup> species are estimated)

Reaction	Log K, 25° C, zero ionic strength	
	Ga	In
$M^{3+} + nOH^- = M(OH)_n^{3-n}, n = 1$	11.6	10.1
2	21.8	20.2
3	31.7	29.5
4	39.4	33.8
$M(OH)_3(am) = M^{3+} + 3OH^-$	37.	N
$M(OH)_3(cr) = M^{3+} + 3OH^-$	N	36.9
$MO(OH)(cr) + H_2O = M^{3+} + 3OH^-$	39.1	N
$M^{3+} + nCN^- = M(CN)_n^{3-n}, n = 1$	4.	4.
2	8.	8.
3	11.	11.
4	14.	13.

N No data.

Table D-25.--Standard Gibbs free energies of  
formation of heavy-metal selenides at 25° C

Compound	$-\Delta_f G^\circ$ kJ·mol <sup>-1</sup>	Additional references
ZnSe	174	87
CdSe	141	88
HgSe	38	89
Cu <sub>2</sub> Se	71	90
CuSe	45	98
Ag <sub>2</sub> Se	51	
AuSe	10	
NiSe	76	91
NiSe <sub>2</sub>	112	91
PbSe	99	92



## APPENDIX E.—EQUILIBRIUM PREDOMINANCE AREA DIAGRAMS

This appendix contains a compilation of equilibrium predominance area diagrams (EPAD). Information on their construction, capabilities, limitations, and use is given in chapters 4 and 11. The diagrams presented here were selected for usefulness in precious metals processing and mine closure operations. All of the diagrams are drawn for a temperature of 25° C and a pressure of 100 kPa (1 bar).

Diagrams are included for free cyanide and carbonate (figures E-1 and E-2), which show selected partial-pressure isobars for HCN and CO<sub>2</sub>, respectively. The Eh-pH diagram for NCO<sup>-</sup>/CN<sup>-</sup> is also included (figure E-3).

A few selected Eh-pH diagrams for sulfur and selenium in the absence and presence of cyanide (figures E-4 through E-9) are included, and they show the conditions under which SCN<sup>-</sup> and SeCN<sup>-</sup> are expected to be stable.

The diagrams for the metal systems compiled in this appendix are summarized in table E-1. As shown in table E-1, pM-pH and pCN-pH diagrams are listed for different values of pCN and pM, respectively. For reference, pCN = 5.0 = 0.26 ppm CN<sup>-</sup>, and pM = 5.0 = 0.65 ppm Zn, 1.12 ppm Cd, 2.01 ppm Hg, 0.64 ppm Cu, 1.08 ppm Ag, 1.97 ppm Au, 0.59 ppm Ni, or 0.56 ppm Fe. The pCN-pH diagrams for solution species show only the predominant solution species regardless of the presence of solid phases. A number of pM-pH and pCN-pH diagrams for selected concentrations of auxiliary species that may exist in process or waste solutions, namely Cl<sup>-</sup>, SCN<sup>-</sup>, S<sub>2</sub>O<sub>3</sub><sup>2-</sup>, CO<sub>3</sub><sup>2-</sup>, and [Fe(CN)<sub>6</sub>]<sup>4-</sup>, are also provided. Also included are pM-pCN

diagrams for selected pH values ranging from 7 to 12. These, along with the pM-pH and pCN-pH diagrams, form the three sets of sections through the pM-pH-pCN composition volume. Some Eh-pH diagrams for pCN = 2.0 and pM = 2.0 are provided; these are compositions typical for precious metals cementation or electrowinning from the pregnant solutions.

No diagrams are given for Cu(II) with CN<sup>-</sup> because Cu(II) is rapidly reduced to Cu(I) cyanide species by CN<sup>-</sup>.

The cyanide chemistry of iron is dominated by the kinetically inert Fe(CN)<sub>6</sub><sup>q-</sup> (q = 3 or 4), so most of the EPAD one might generate for iron would be of limited use at best. For both Fe(II) and Fe(III), pM-pH diagrams with no ligands and with p[Fe(CN)<sub>6</sub><sup>4-</sup>] = 4.0 are provided, as is done for several other metal ions. A pM-pH diagram with pCO<sub>3</sub> = 3.0 is provided for Fe(II), analogous to corresponding diagrams for other divalent metal ions.

Diagrams are not provided for cobalt or chromium because the cyanide chemistry of those metals is kinetically controlled, and EPAD would be of limited, if not misleading, significance. As described in chapter 8, Co(II) in the presence of CN<sup>-</sup> is very easily oxidized by O<sub>2</sub> to the very inert Co(CN)<sub>6</sub><sup>3-</sup>.

Diagrams are not provided for manganese because manganese is of minor importance in cyanide operations, the cyanide complexes of manganese are not very stable, and the data for the manganese cyanide complexes are not known accurately.



Table E-1.-Compilation of equilibrium predominance area diagrams in this appendix<sup>1</sup>

Variables in diagram	Zn 2+	Cd 2+	Hg 2+	Cu 1+	Cu 2+	Ag 1+	Au 1+	Ni 2+
pH-pM, no ligands	y	y	<sup>2</sup> n	<sup>2</sup> n	y	<sup>2</sup> n	<sup>2</sup> n	y
pH-pM, pCO <sub>3</sub> = 3.0	y	y	<sup>3</sup> n	<sup>3</sup> n	y	<sup>3</sup> n	<sup>3</sup> n	y
pH-pM, pCN = 2.0, 3.0, 4.0, 5.0	y	y	y	y	<sup>4</sup> n	y	y	y
pH-pM, pCN = 2.0, pSH = 6.0	y	y	y	y	<sup>4</sup> n	y	<sup>2</sup> n	y
pH-pM, pCN = 5.0, pCO <sub>3</sub> = 3.0	y	y	<sup>3</sup> n	<sup>3</sup> n	<sup>4</sup> n	<sup>3</sup> n	<sup>3</sup> n	y
pH-pM, pCN = 5.0, pCl = 3.0	<sup>3</sup> n	<sup>3</sup> n	y	<sup>3</sup> n	<sup>4</sup> n	y	<sup>3</sup> n	<sup>3</sup> n
pH-pM, pCN = 5.0, pSCN = 4.0	<sup>3</sup> n	<sup>3</sup> n	y	y	<sup>4</sup> n	y	y	<sup>3</sup> n
pH-pM, pCN = 5.0, pS <sub>2</sub> O <sub>3</sub> = 4.0	<sup>3</sup> n	<sup>3</sup> n	y	y	<sup>4</sup> n	y	y	<sup>3</sup> n
pH-pM, pCN = 5.0, p[Fe(CN) <sub>6</sub> <sup>4-</sup> ] = 4.0	y	y	<sup>5</sup> n	<sup>5</sup> n	y	<sup>5</sup> n	<sup>5</sup> n	y
pCN-pH, solution species only	y	y	y	y	<sup>4</sup> n	y	y	y
pCN-pH, pM = 2.0, 3.0, 4.0, 5.0	y	y	<sup>6</sup> y	y	<sup>4</sup> n	y	y	y
pCN-pH, pM = 4.0, p[Fe(CN) <sub>6</sub> <sup>4-</sup> ] = 4.0	y	y	<sup>5</sup> n	<sup>5</sup> n	<sup>4</sup> n	<sup>5</sup> n	<sup>5</sup> n	y
pCN-pH, pCl = 3.0, solution species only	<sup>3</sup> n	<sup>3</sup> n	y	<sup>3</sup> n	<sup>4</sup> n	y	y	<sup>3</sup> n
pCN-pH, pSCN = 4.0, solution species only	<sup>3</sup> n	<sup>3</sup> n	y	y	<sup>4</sup> n	y	y	<sup>3</sup> n
pCN-pH, pS <sub>2</sub> O <sub>3</sub> = 4.0, solution species only	<sup>3</sup> n	<sup>3</sup> n	y	y	<sup>4</sup> n	y	y	<sup>3</sup> n
pM-pCN, pH = 12.0, 11.0, 10.0, 9.0, 8.0, 7.0	y	y	y	y	<sup>4</sup> n	<sup>7</sup> y	<sup>7</sup> y	y
Eh-pH, pM = 2.0, pCN = 2.0	y	y	y	<sup>8</sup> n	y	y	y	y

<sup>1</sup>y = diagram included, n = diagram not included.<sup>2</sup>Diagram is of no practical importance.<sup>3</sup>Species containing auxiliary ligand do not appear in diagram.<sup>4</sup>Redox reactions occur.<sup>5</sup>Uncomplexed metal cation and [Fe(CN)<sub>6</sub>]<sup>4-</sup> are unstable with respect to removal of CN<sup>-</sup> from [Fe(CN)<sub>6</sub>]<sup>4-</sup> by the metal cation.<sup>6</sup>Diagrams for pHg = 4.0 and 5.0 are the same as the diagram for solution species only.<sup>7</sup>Diagrams for pH 12.0 and 10.0 are the same as the diagram for pH 11.0.<sup>8</sup>See the diagram for Cu(II).



Figure E-1

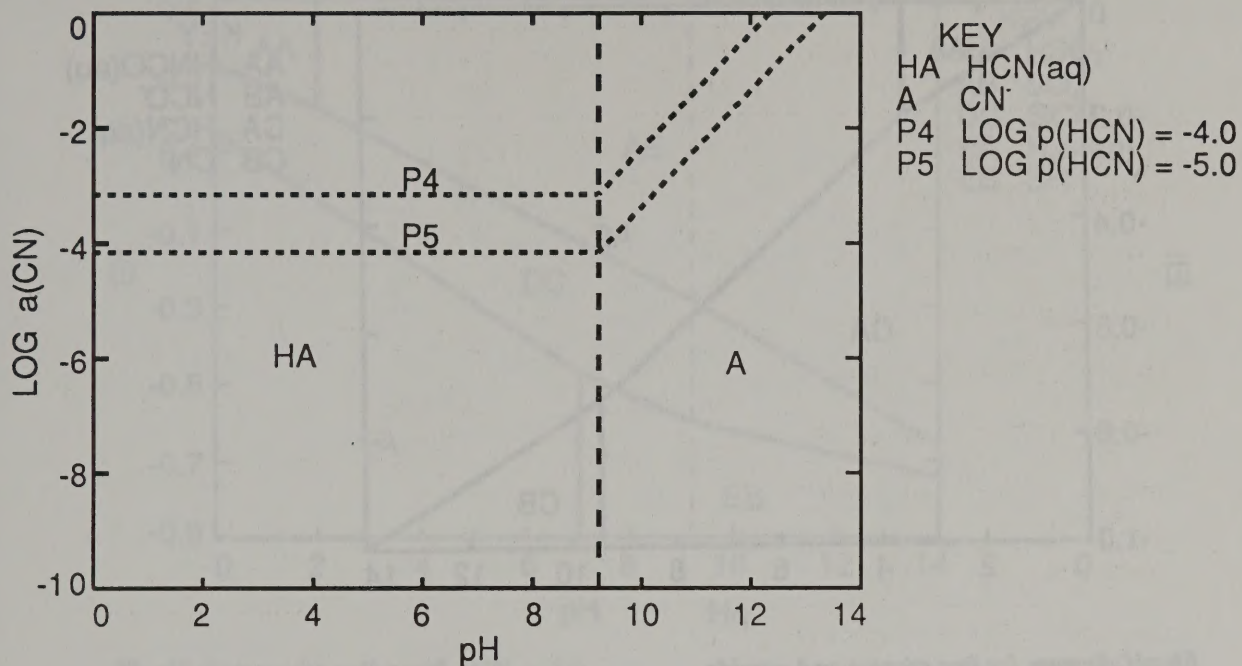
*pL-pH diagram for free cyanide.*

Figure E-2

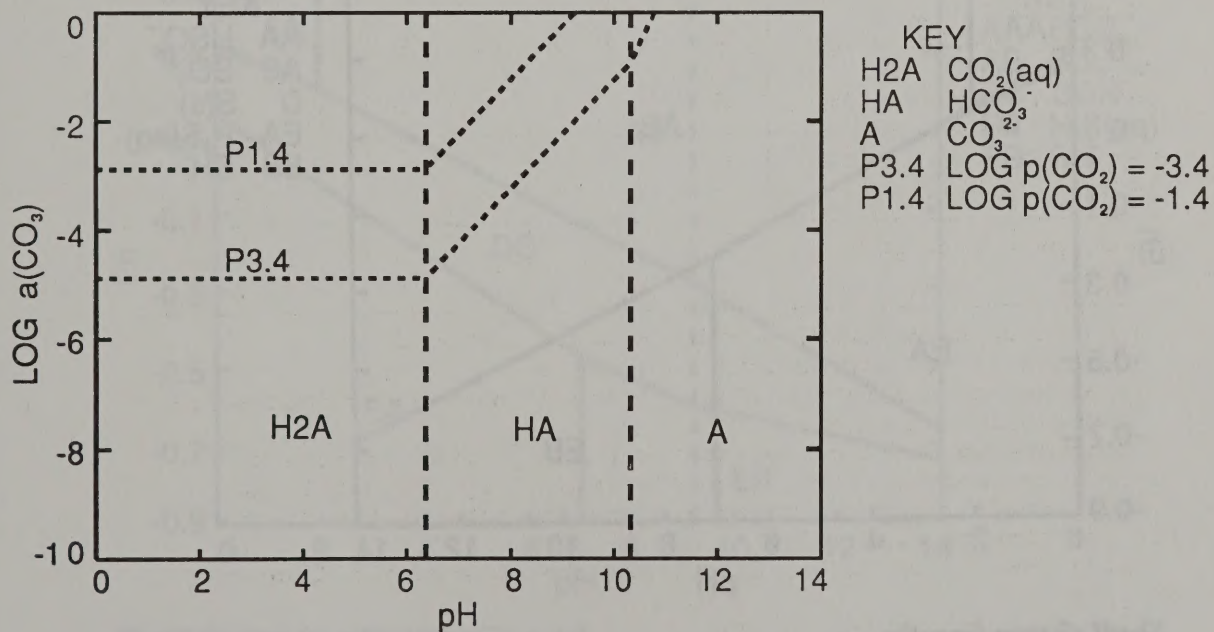
*pL-pH diagram for free carbonic acid.*



Figure E-3

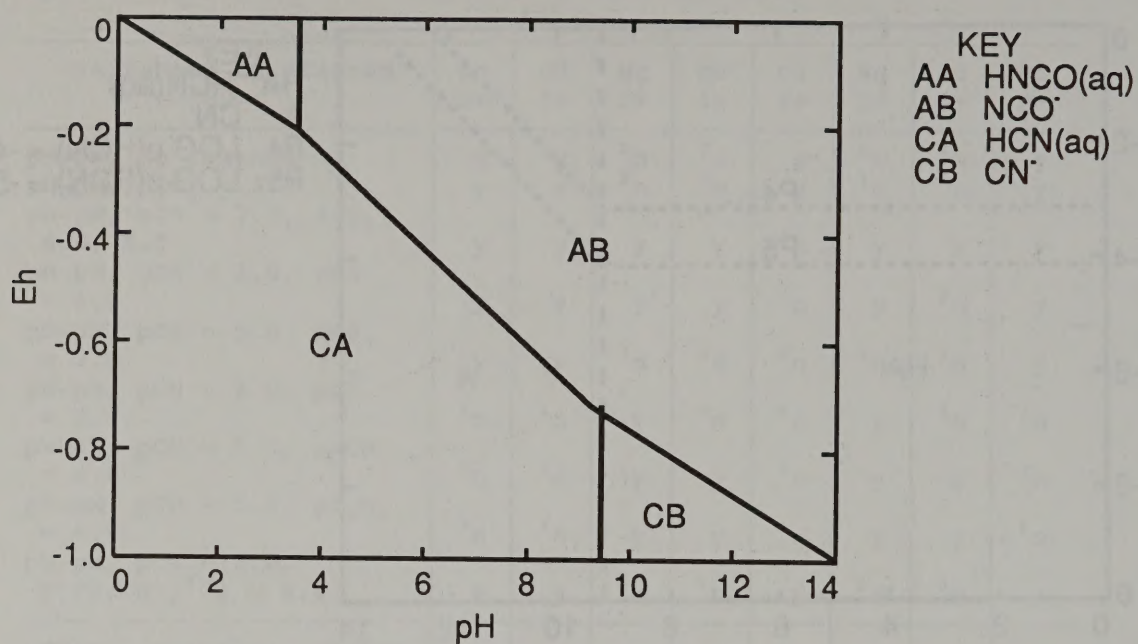
*Eh-pH diagram for free cyanate and cyanide.*

Figure E-4

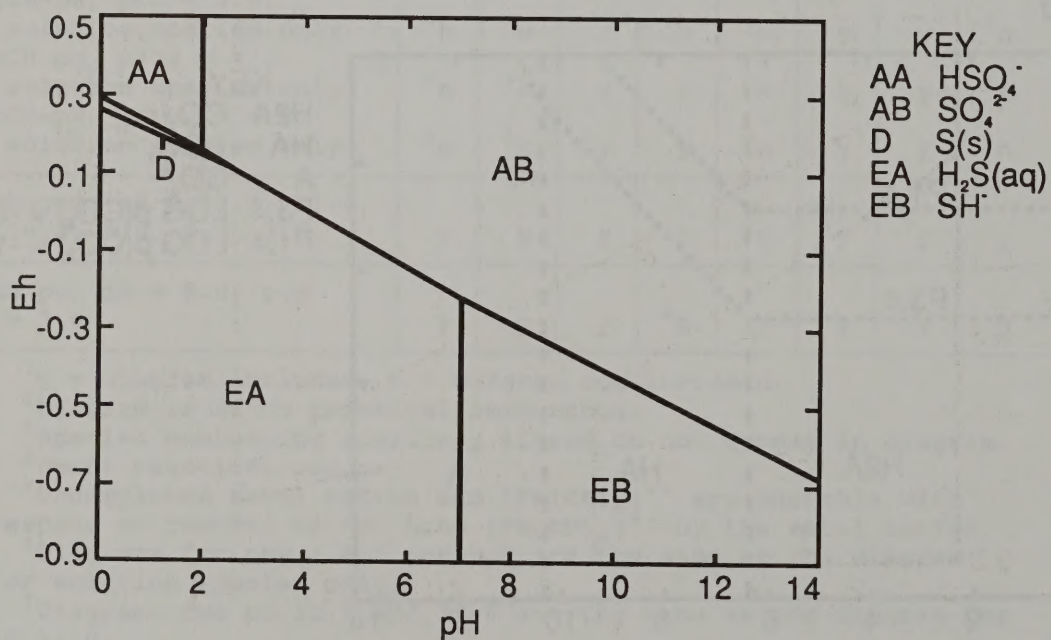
*Eh-pH diagram for sulfur.*



Figure E-5

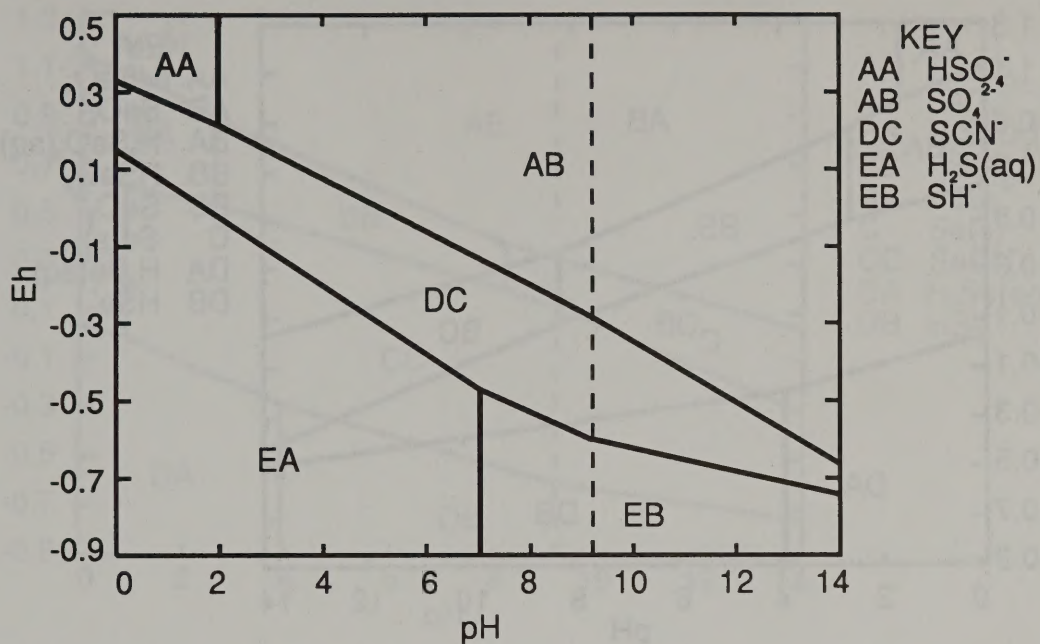
*Eh-pH diagram for sulfur with  $p\text{CN} = 5.0$ .*

Figure E-6

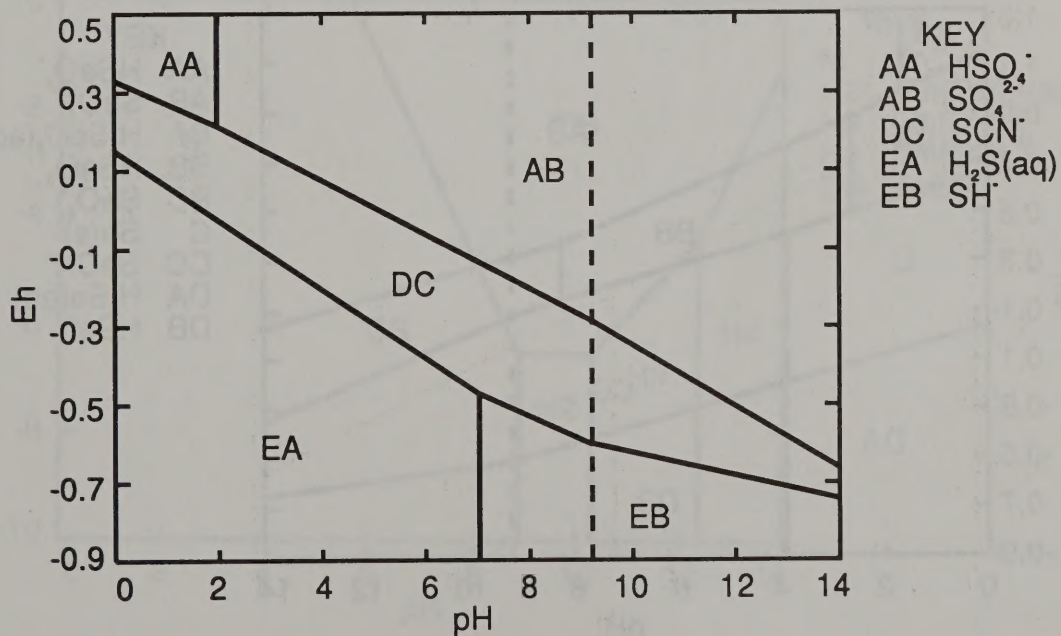
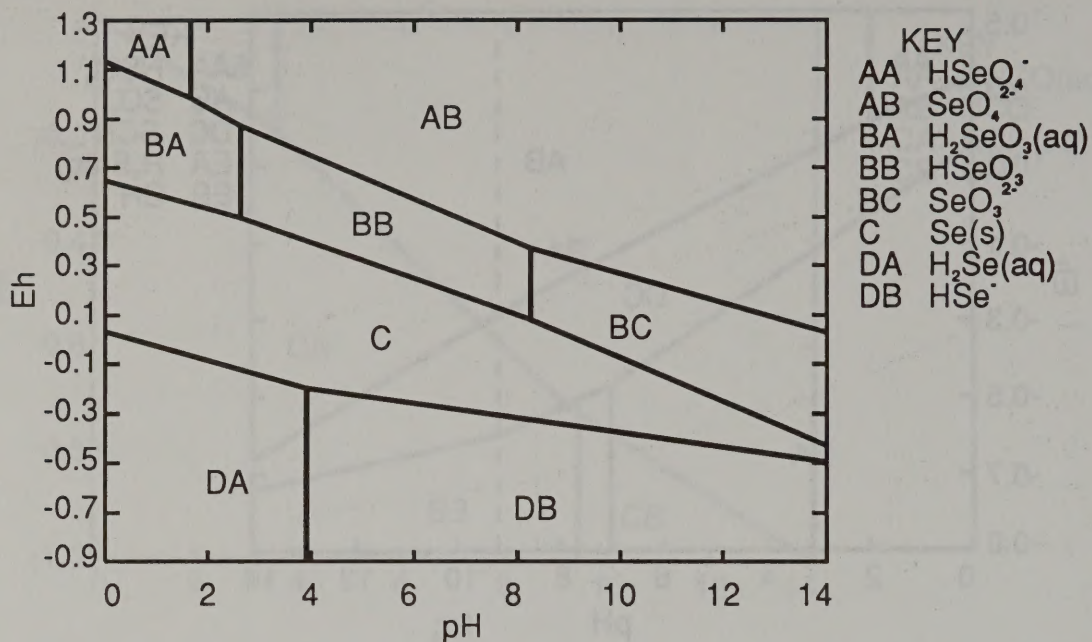
*Eh-pH diagram for sulfur with  $p\text{CN} = 2.0$ .*



Figure E-7



Eh-pH diagram for selenium.

Figure E-8

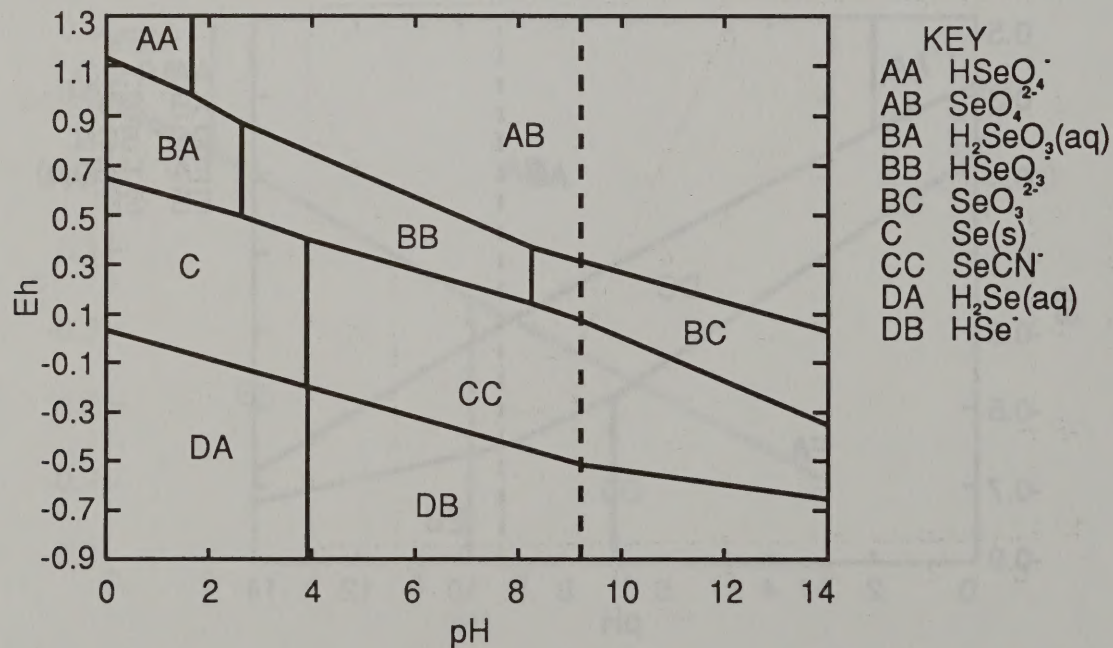
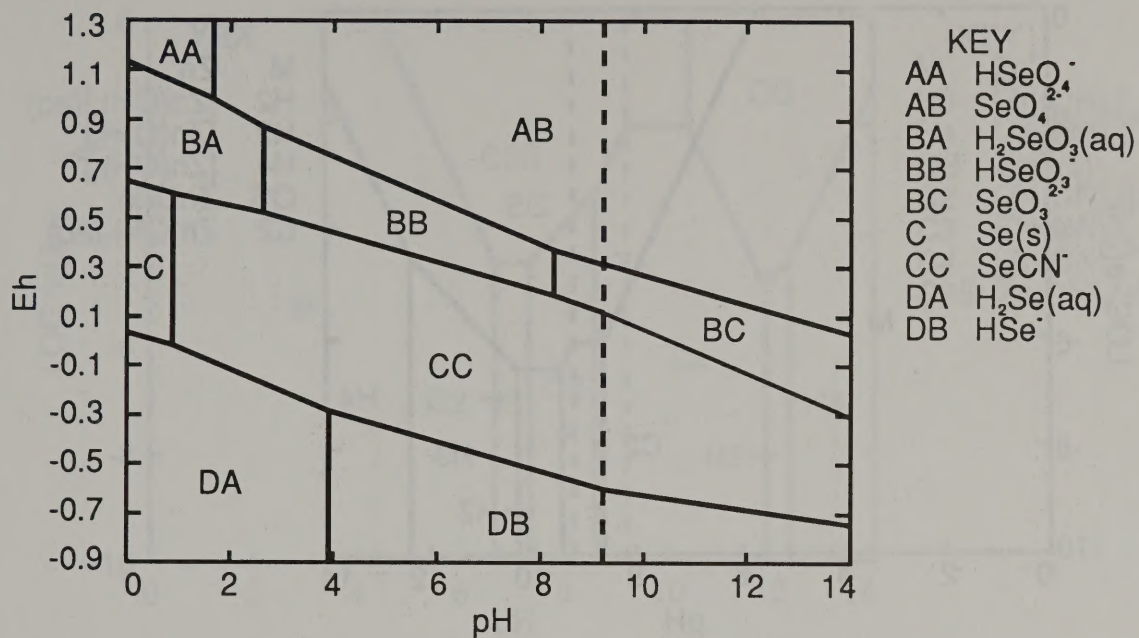
Eh-pH diagram for selenium with  $p\text{CN} = 5.0$ .

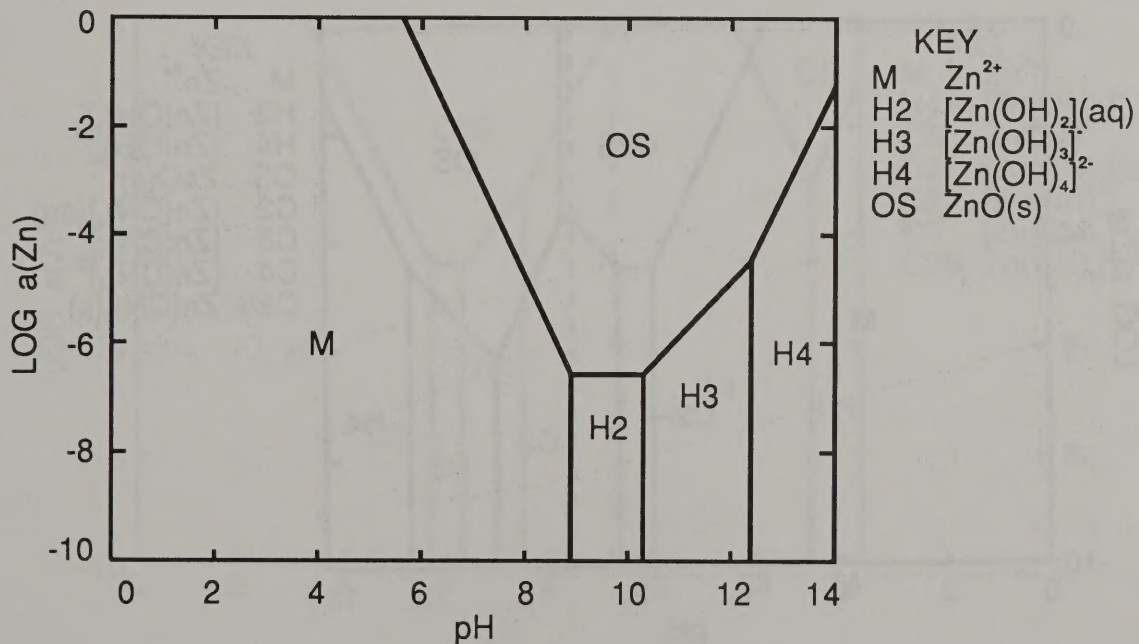


Figure E-9



*Eh-pH diagram for selenium with  $p\text{CN} = 2.0$ .*

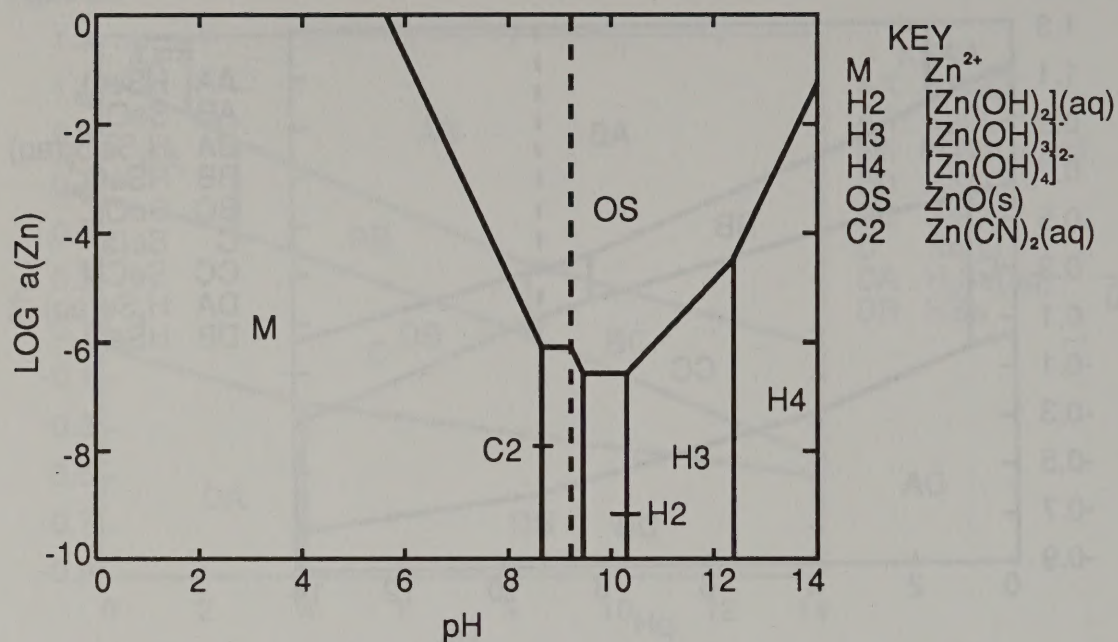
Figure E-10



*pZn-pH diagram with no ligands.*

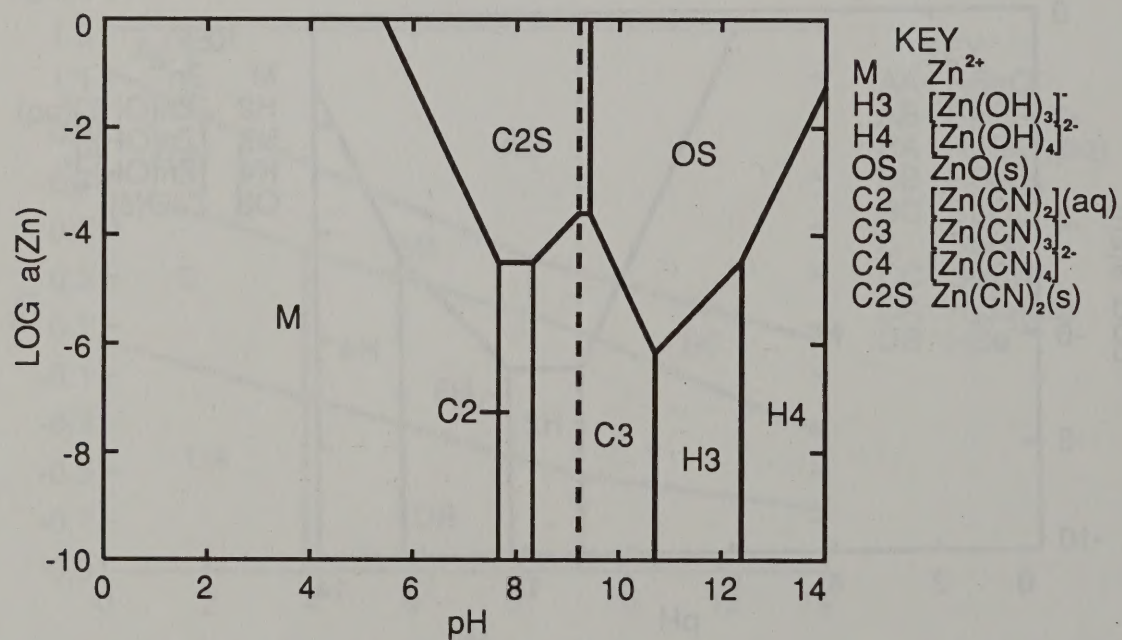


Figure E-11



*pZn-pH diagram for  $p\text{CN} = 5.0$ .*

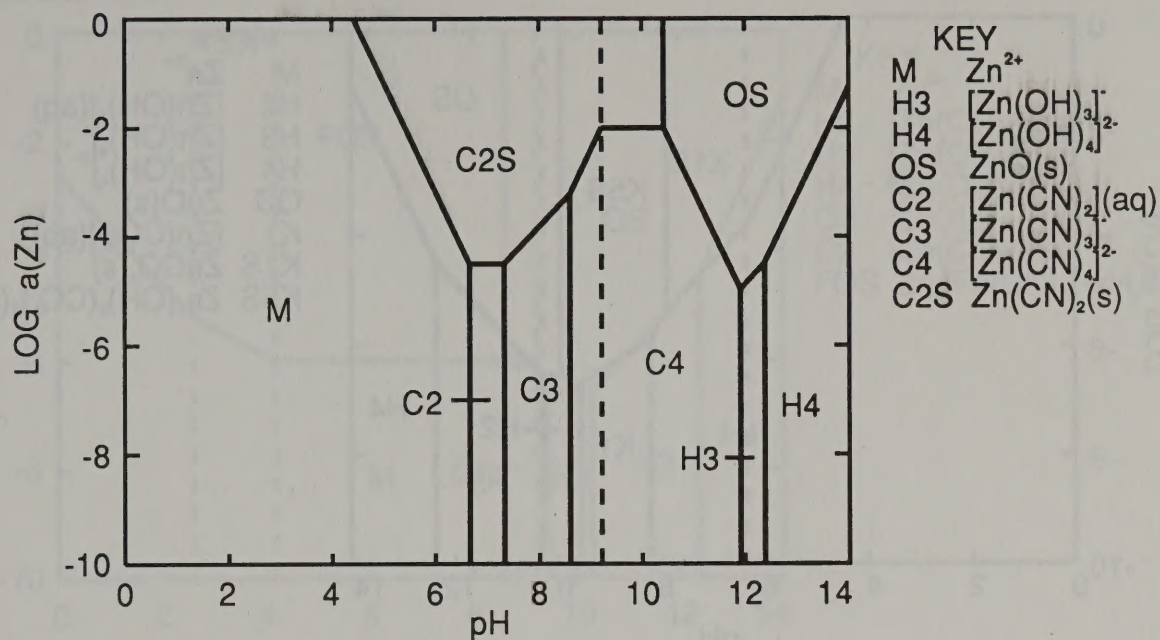
Figure E-12



*pZn-pH diagram for  $p\text{CN} = 4.0$ .*

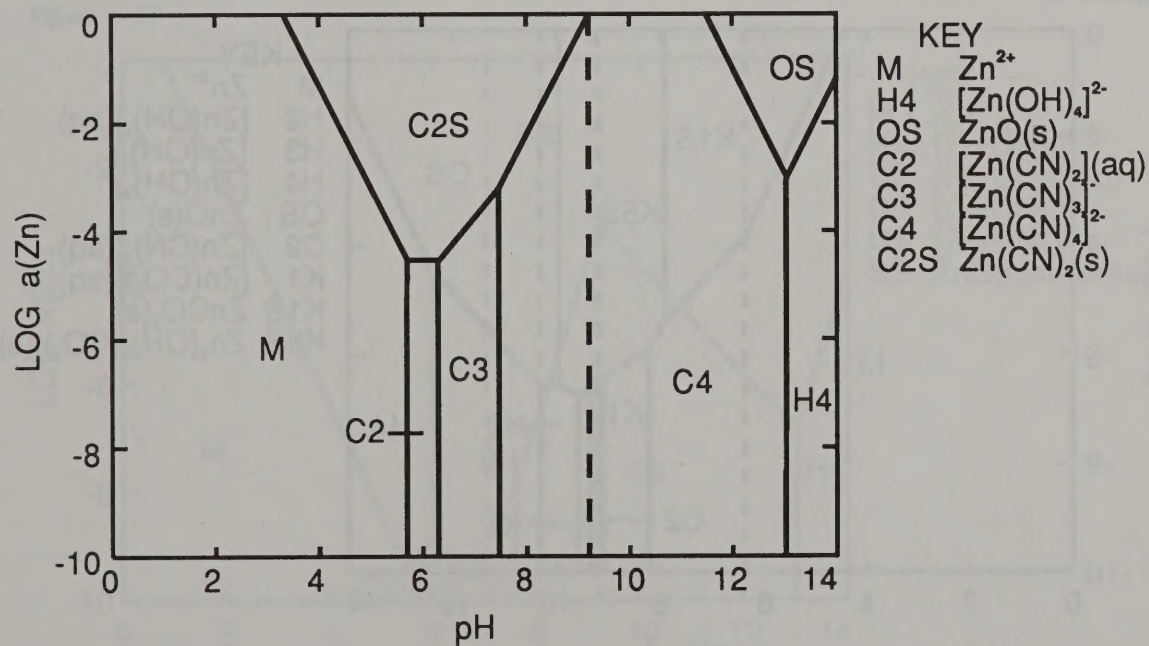


Figure E-13



*pZn-pH diagram for  $p\text{CN} = 3.0$ .*

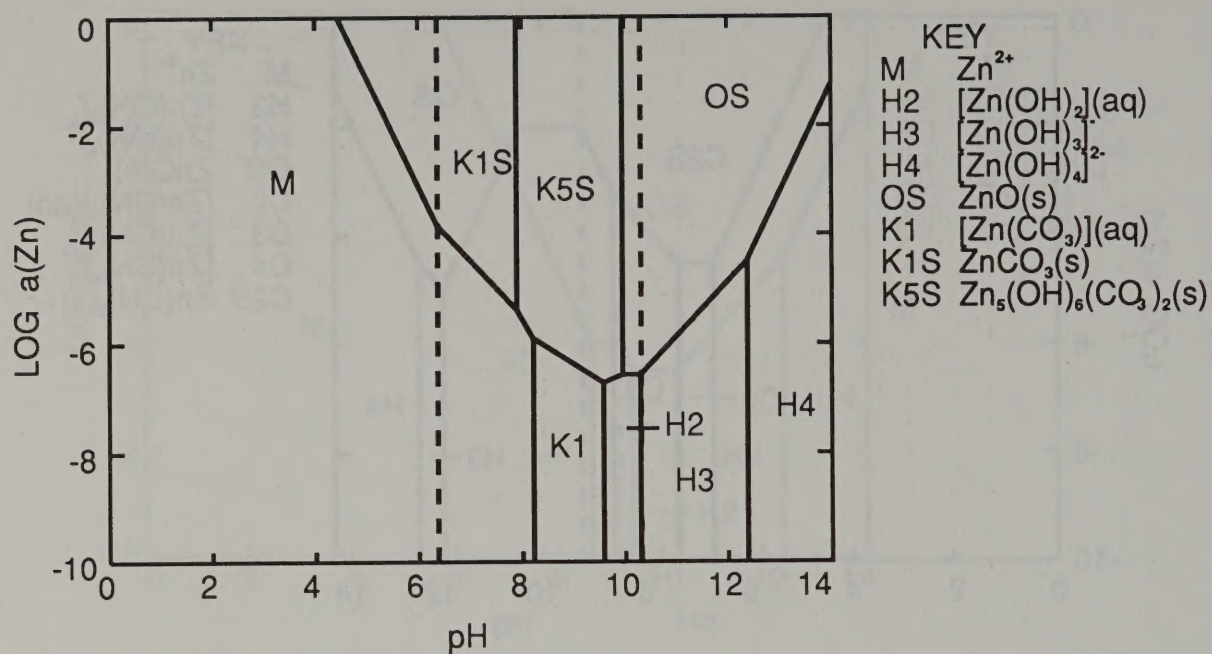
Figure E-14



*pZn-pH diagram for  $p\text{CN} = 2.0$ .*

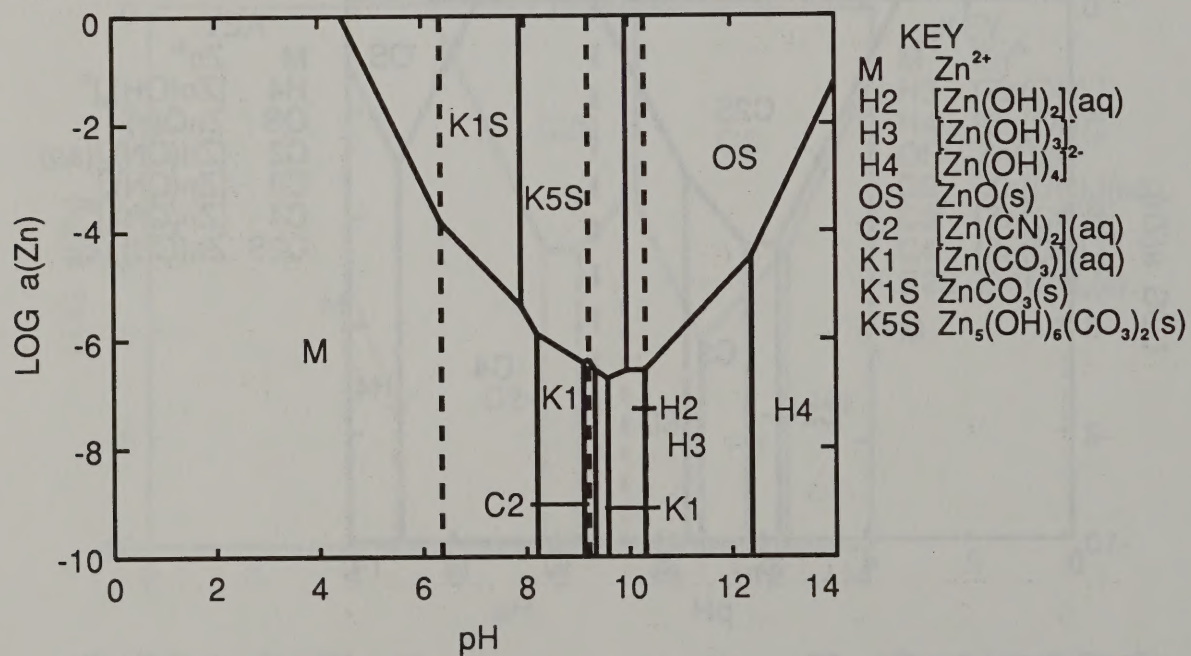


Figure E-15



*pZn-pH diagram for  $p\text{CO}_3 = 3.0$ .*

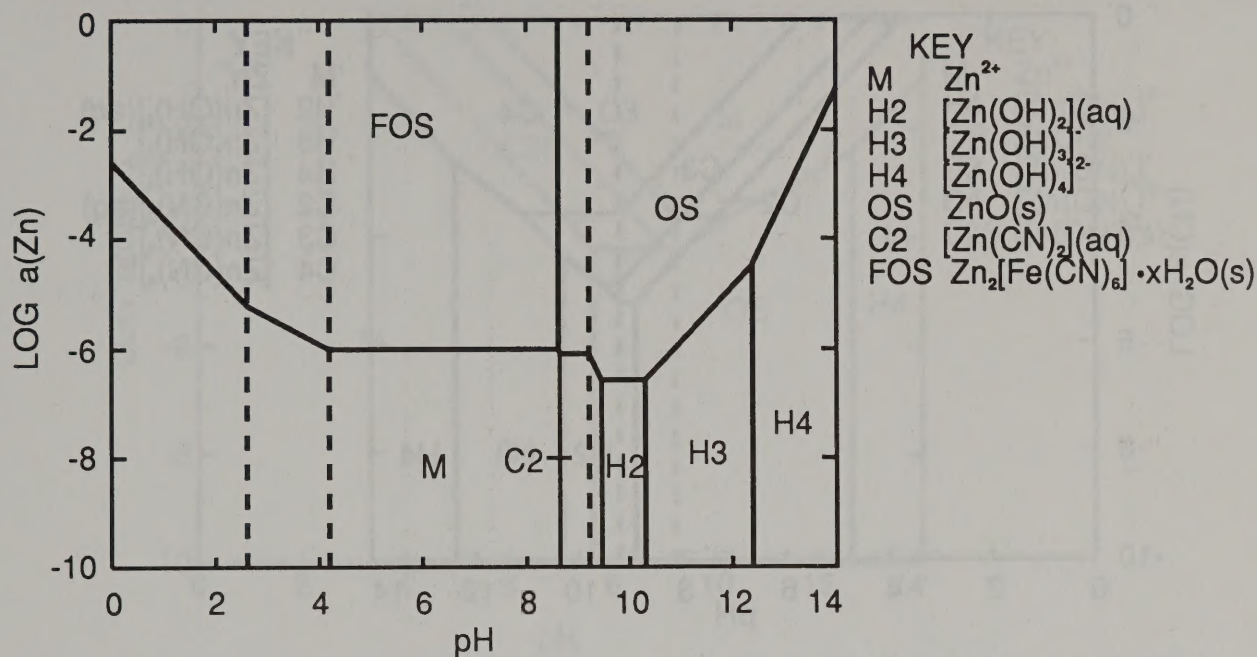
Figure E-16



*pZn-pH diagram for  $p\text{CN} = 5.0$  and  $p\text{CO}_3 = 3.0$ .*

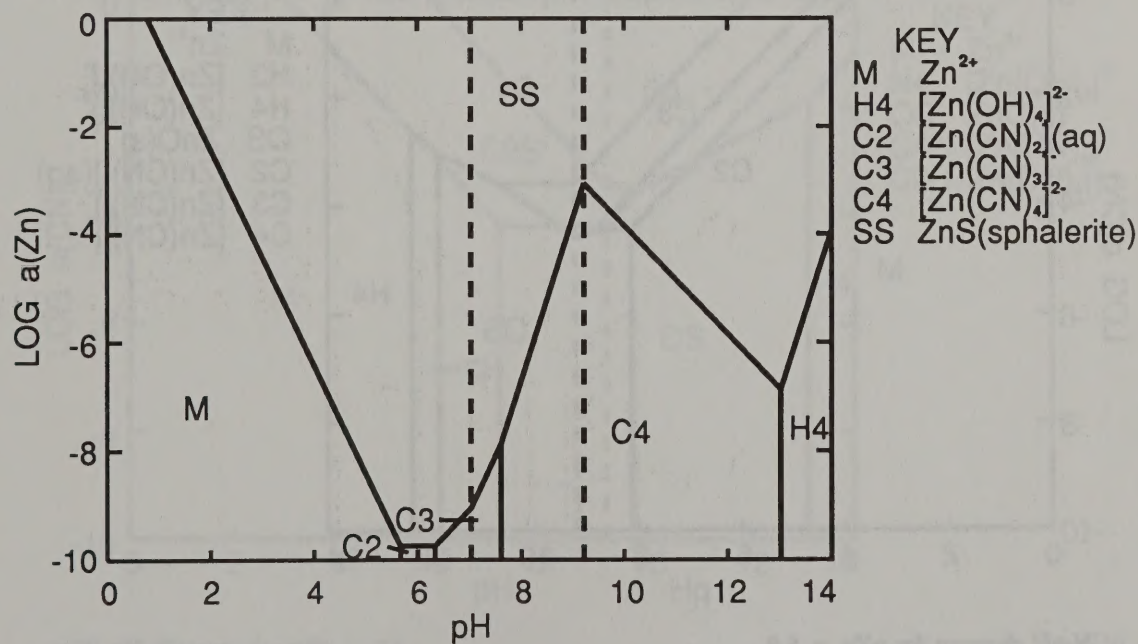


Figure E-17



*pZn-pH diagram for  $p\text{CN} = 5.0$  and  $p[\text{Fe}(\text{CN})_6^{4-}] = 4.0$ .*

Figure E-18



*pZn-pH diagram for  $p\text{CN} = 2.0$  and  $p\text{SH} = 6.0$ .*



Figure E-19

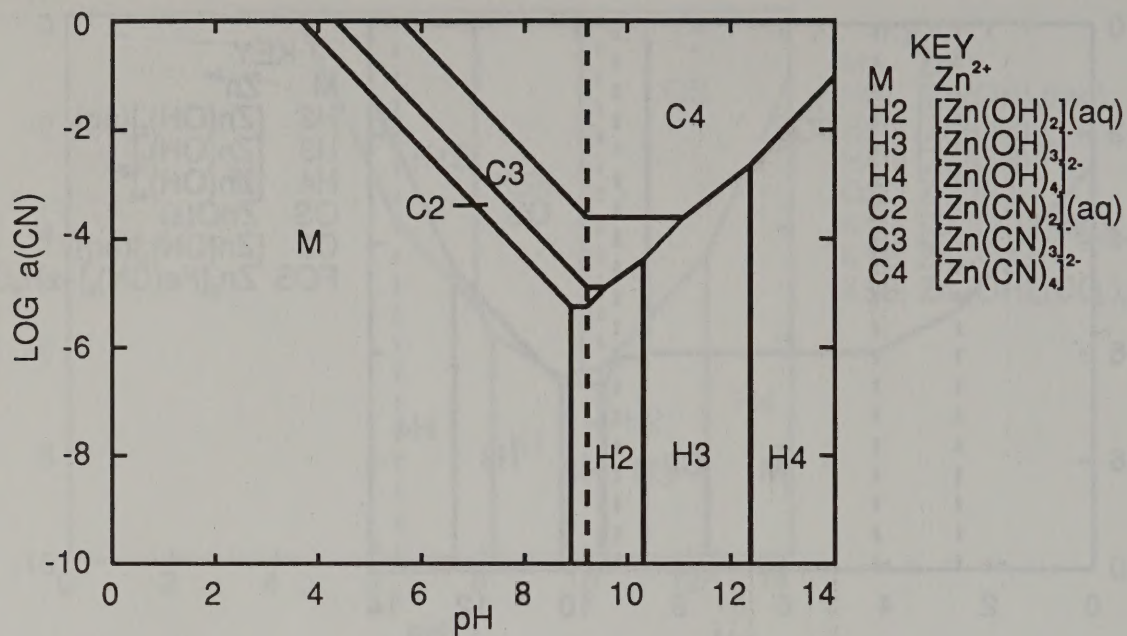
*pCN-pH diagram for zinc solution species.*

Figure E-20

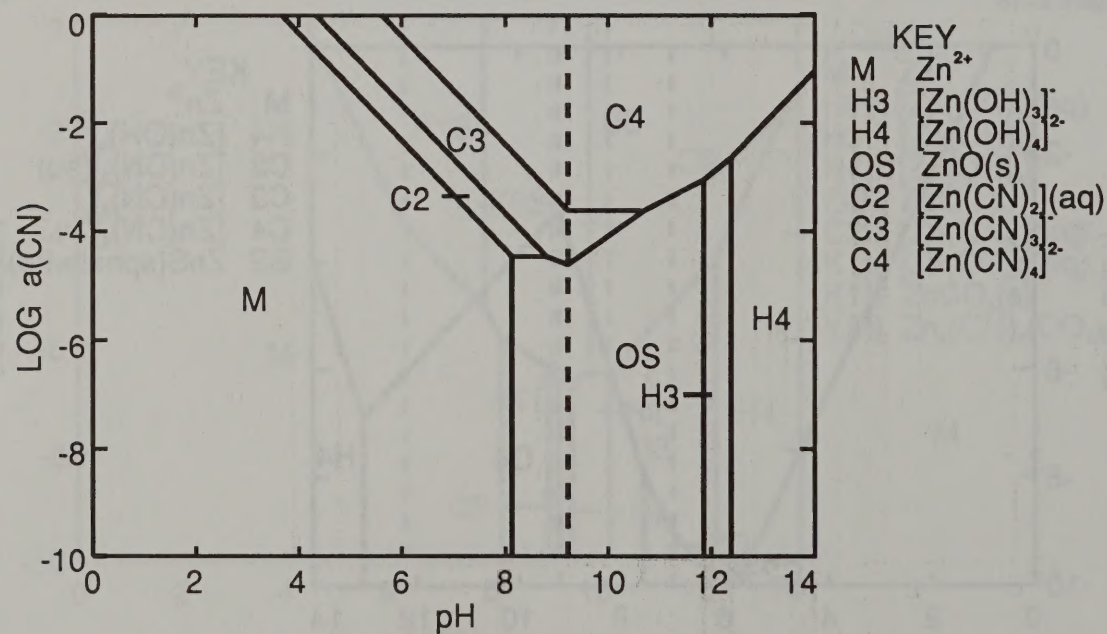
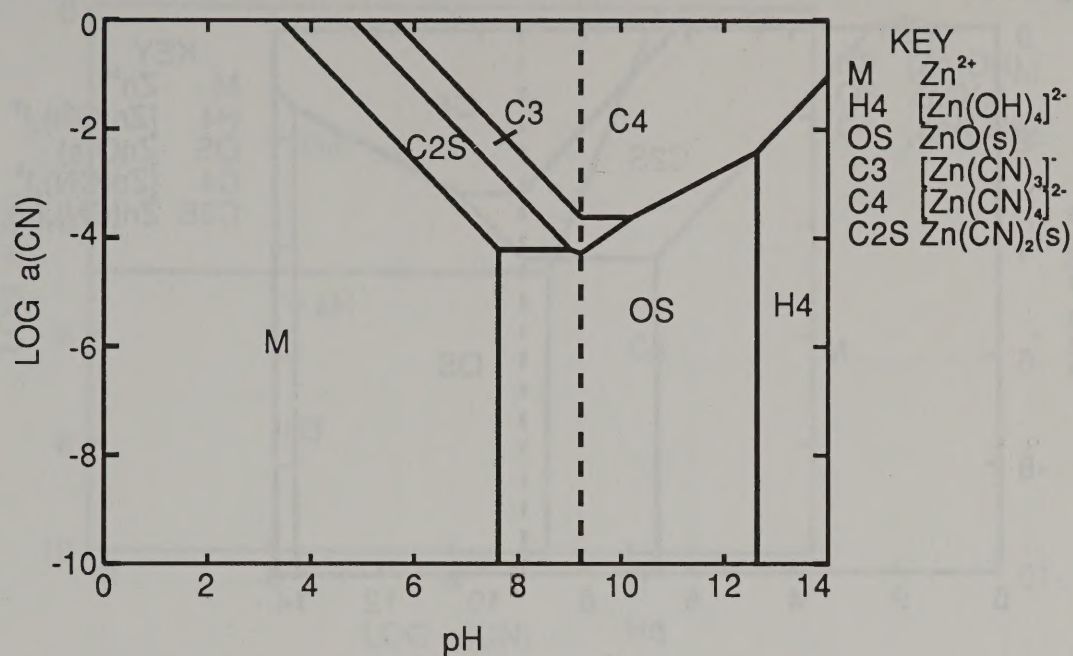
*pCN-pH diagram for  $p\text{Zn} = 5.0$ .*

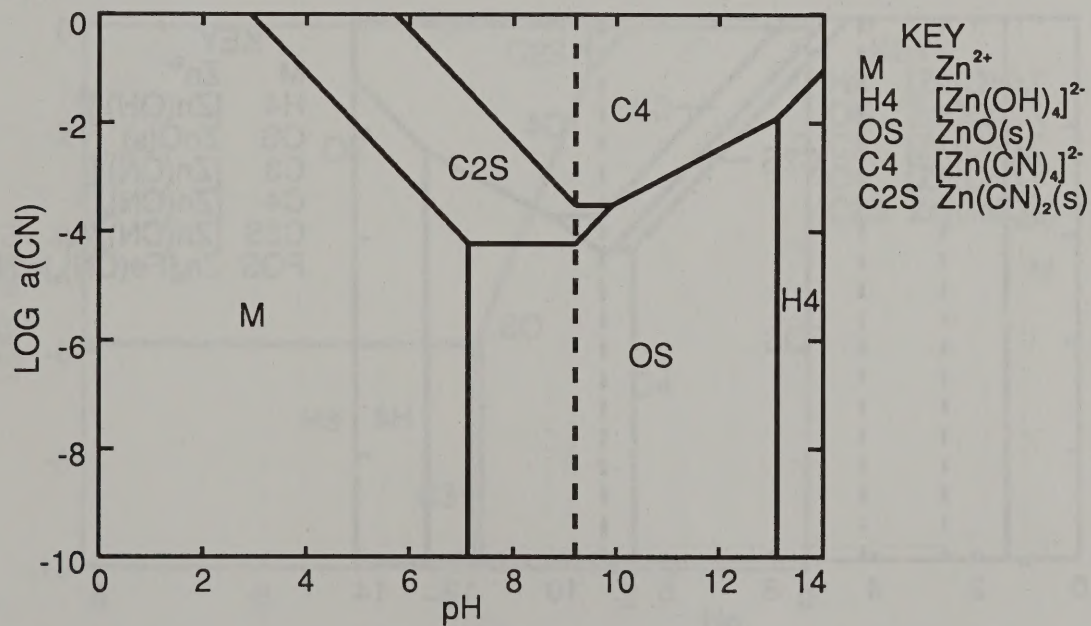


Figure E-21



*pCN-pH diagram for  $pZn = 4.0$ .*

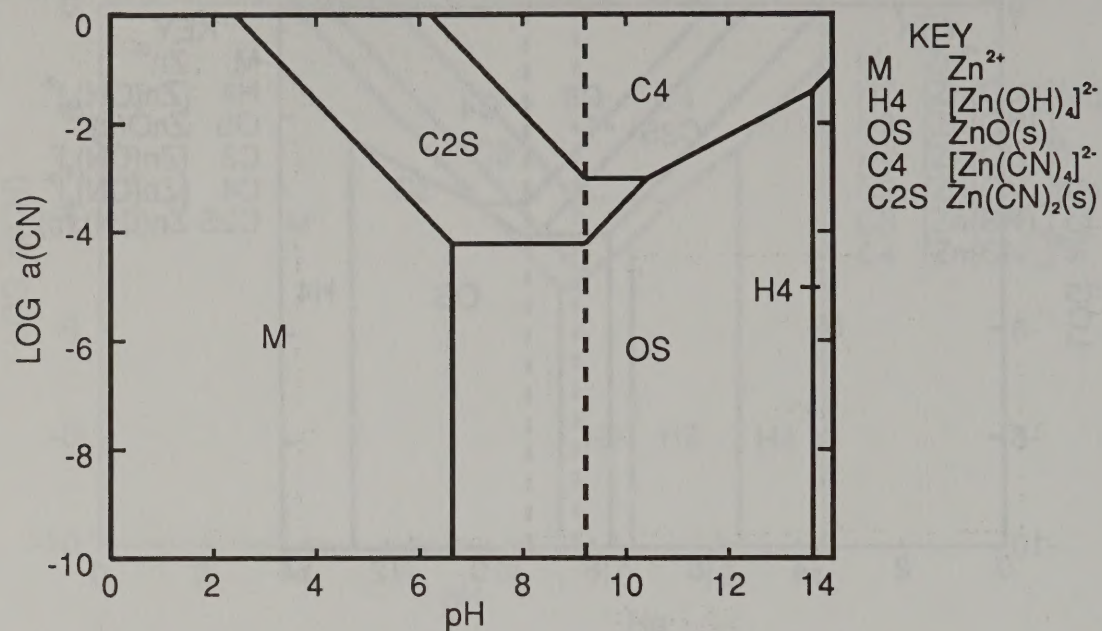
Figure E-22



*pCN-pH diagram for  $pZn = 3.0$ .*

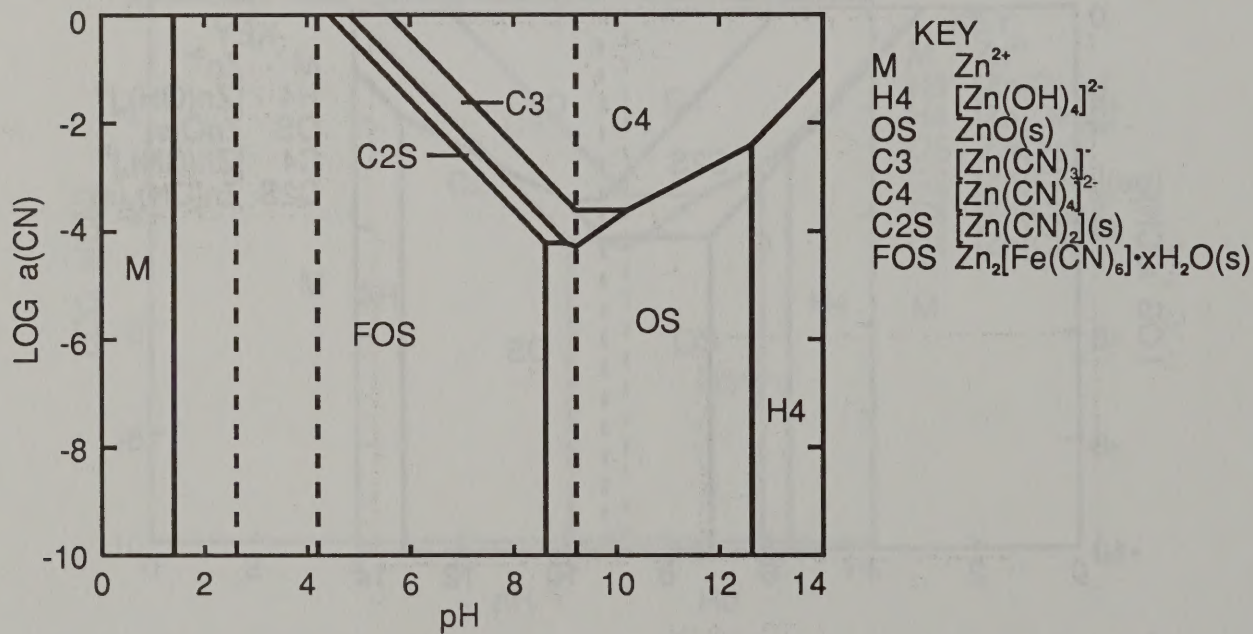


Figure E-23



*pCN-pH diagram for  $p\text{Zn} = 2.0$ .*

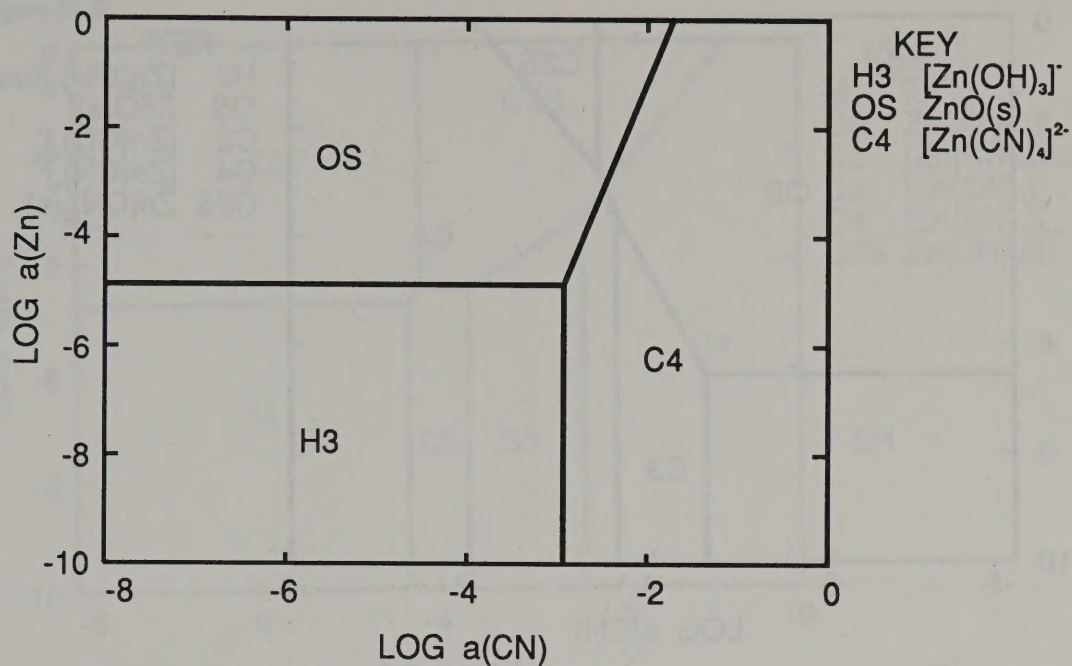
Figure E-24



*pCN-pH diagram for  $p\text{Zn} = 4.0$  and  $p[\text{Fe}(\text{CN})_6]^{4-} = 4.0$ .*

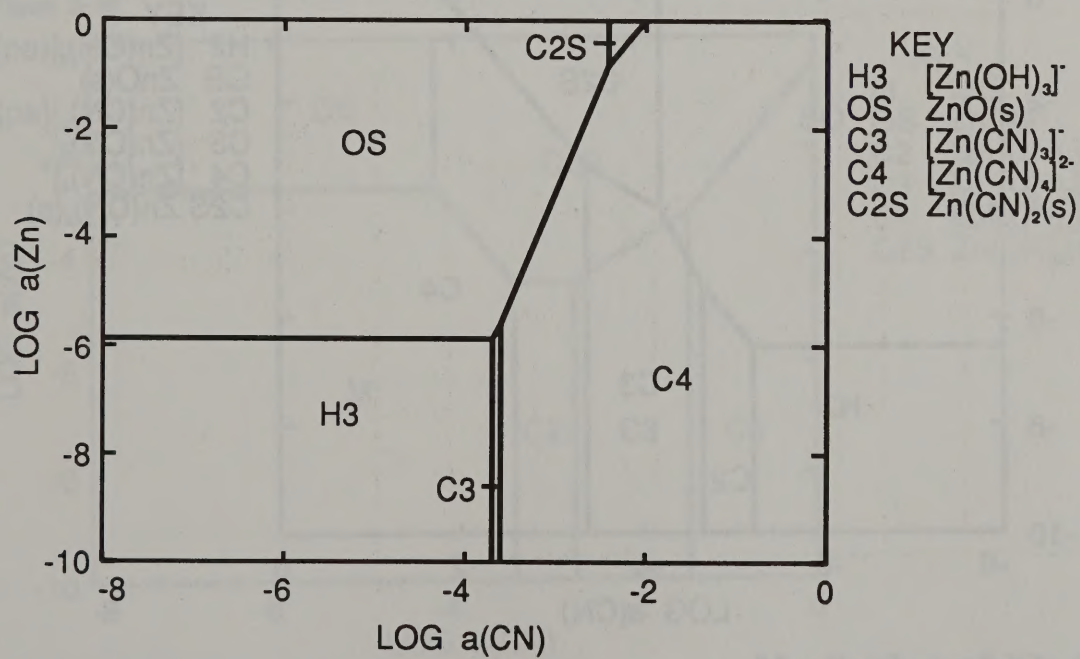


Figure E-25



$pZn$ - $pCN$  diagram for  $pH = 12.0$ .

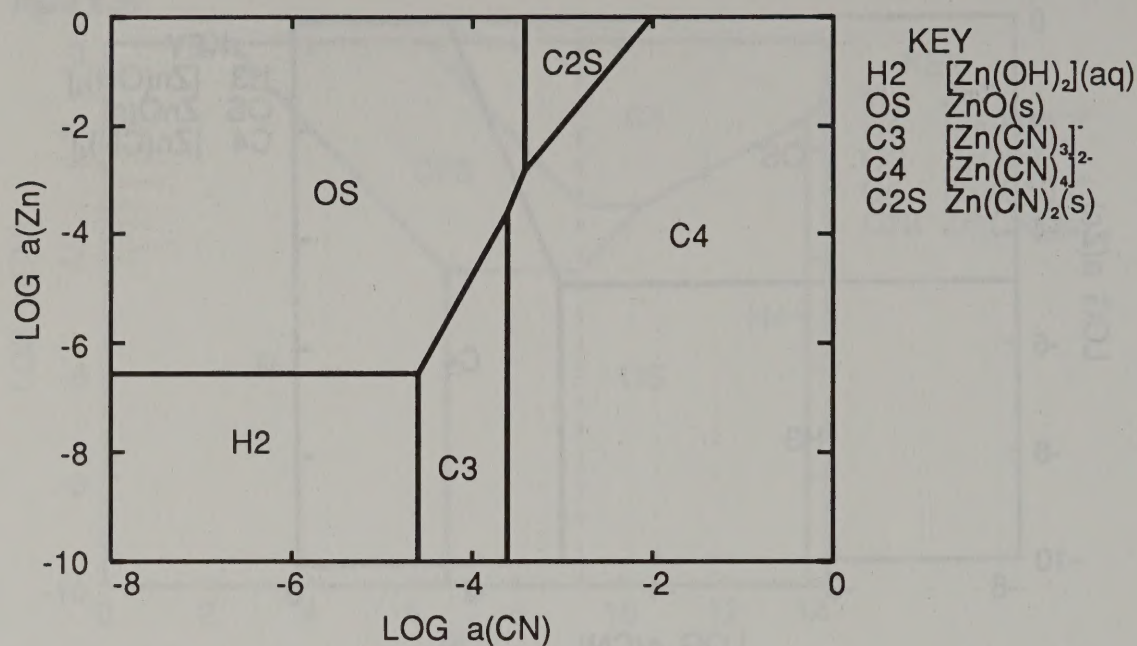
Figure E-26



$pZn$ - $pCN$  diagram for  $pH = 11.0$ .

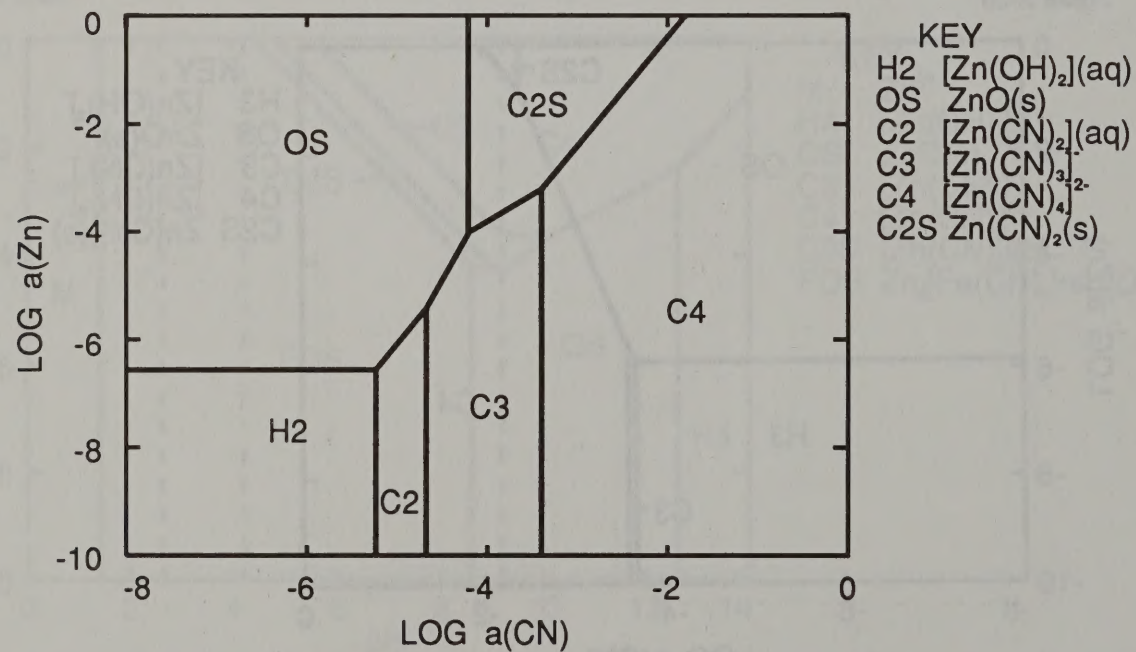


Figure E-27



*pZn-pCN diagram for pH = 10.0.*

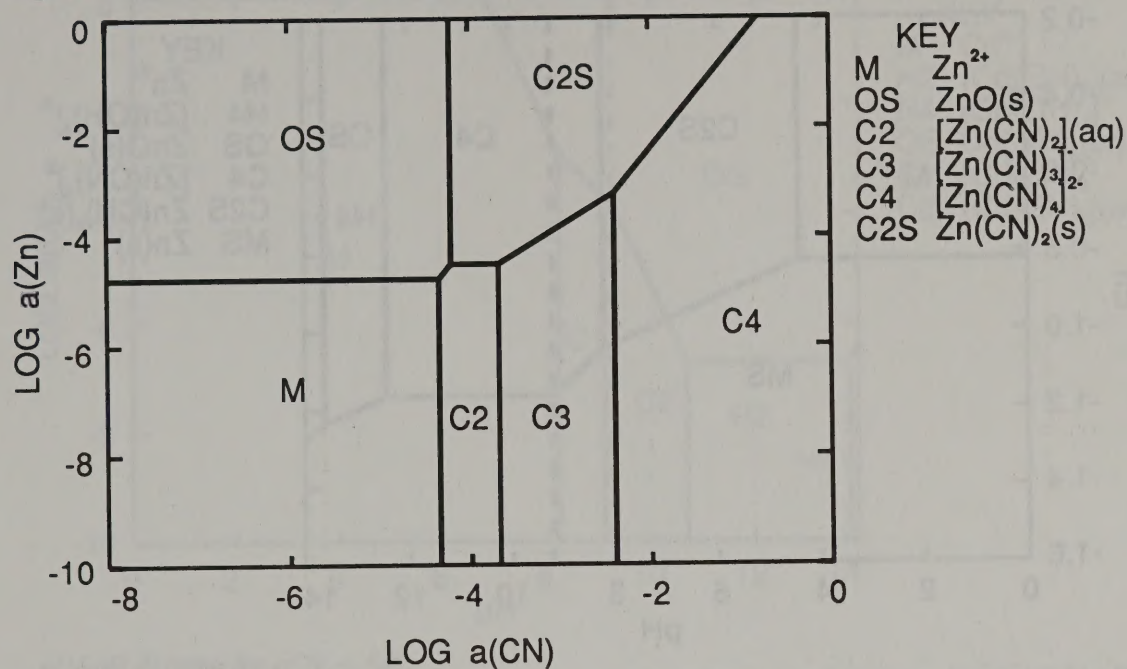
Figure E-28



*pZn-pCN diagram for pH = 9.0.*

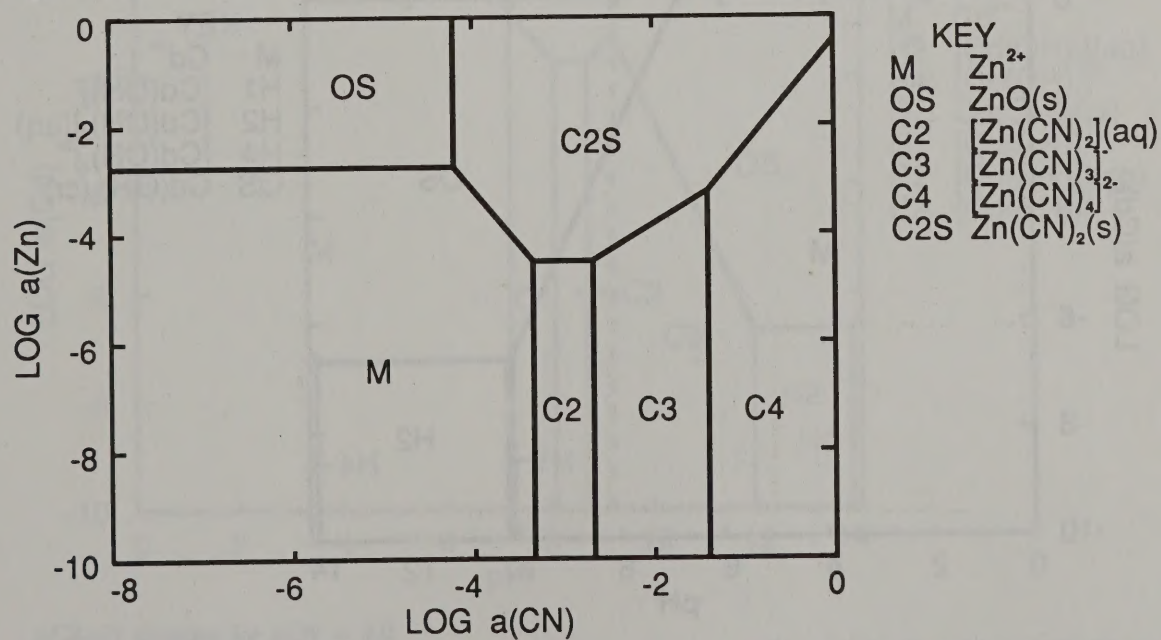


Figure E-29



$pZn$ - $pCN$  diagram for  $pH = 8.0$ .

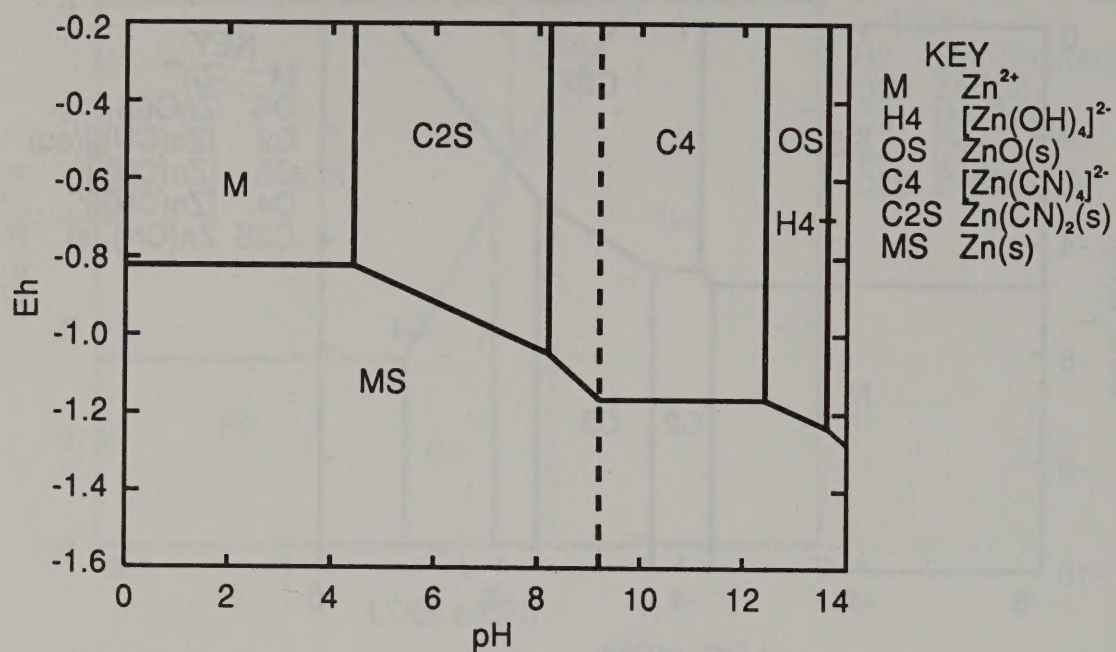
Figure E-30



$pZn$ - $pCN$  diagram for  $pH = 7.0$ .

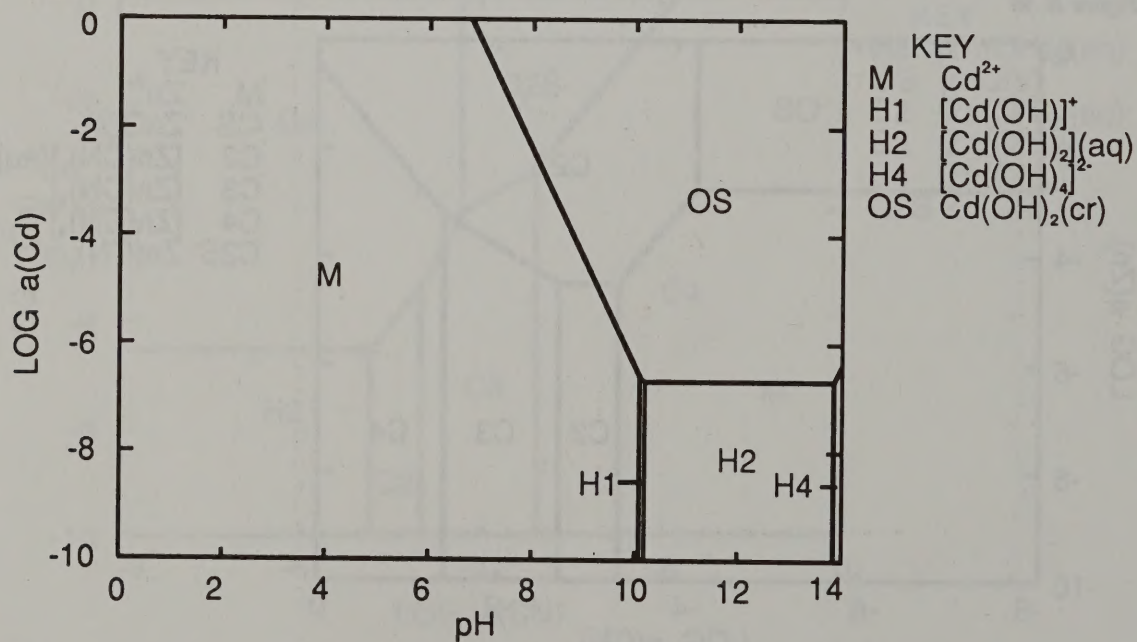


Figure E-31



*Eh-pH diagram for  $p\text{Zn} = 2.0$  and  $p\text{CN} = 2.0$ .*

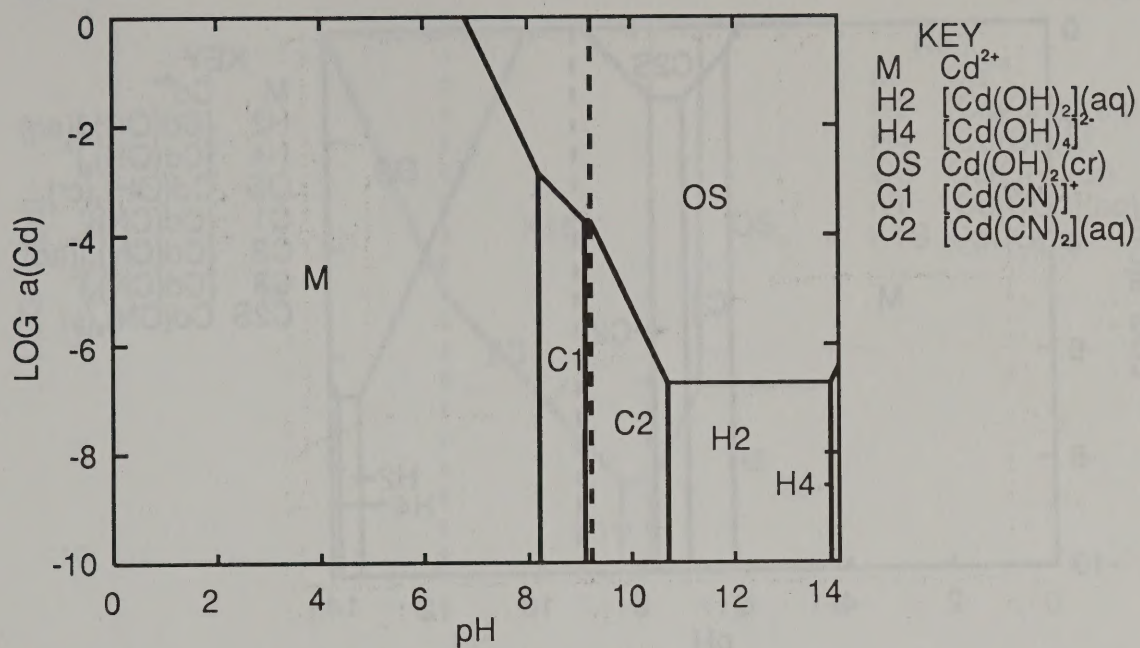
Figure E-32



*pCd-pH diagram with no ligands.*

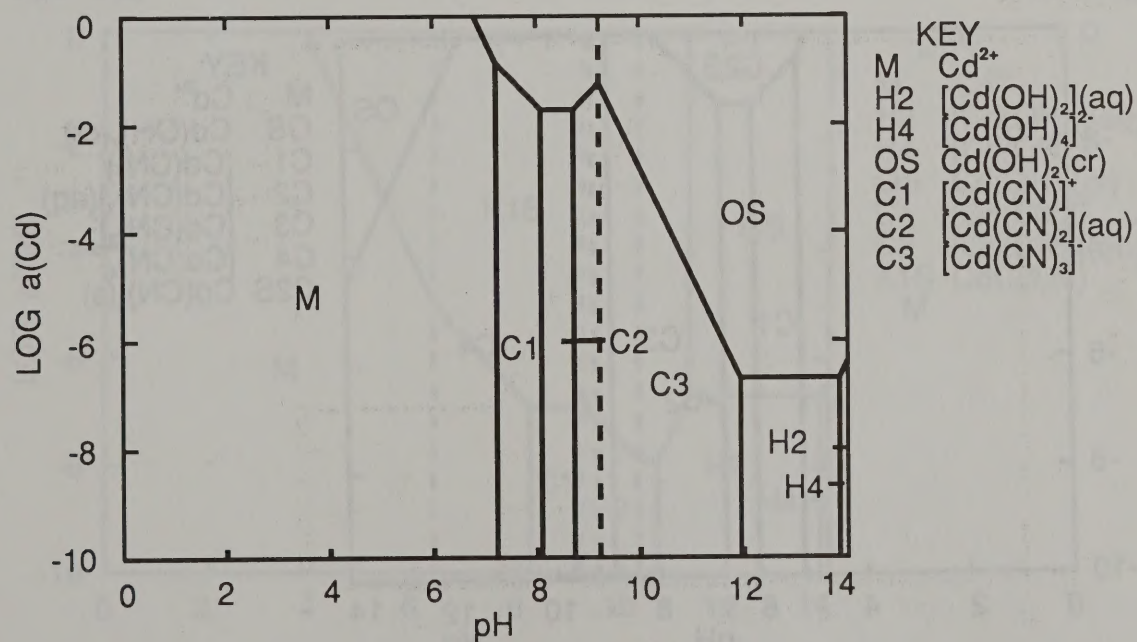


Figure E-33



*pCd-pH diagram for  $p\text{CN} = 5.0$ .*

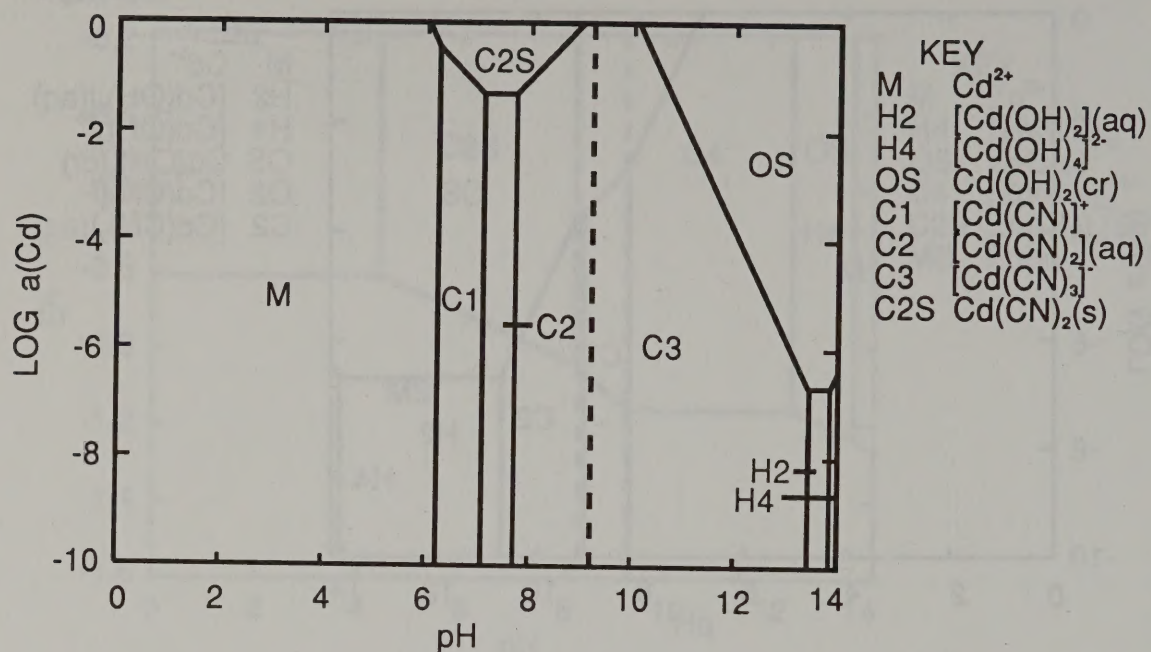
Figure E-34



*pCd-pH diagram for  $p\text{CN} = 4.0$ .*

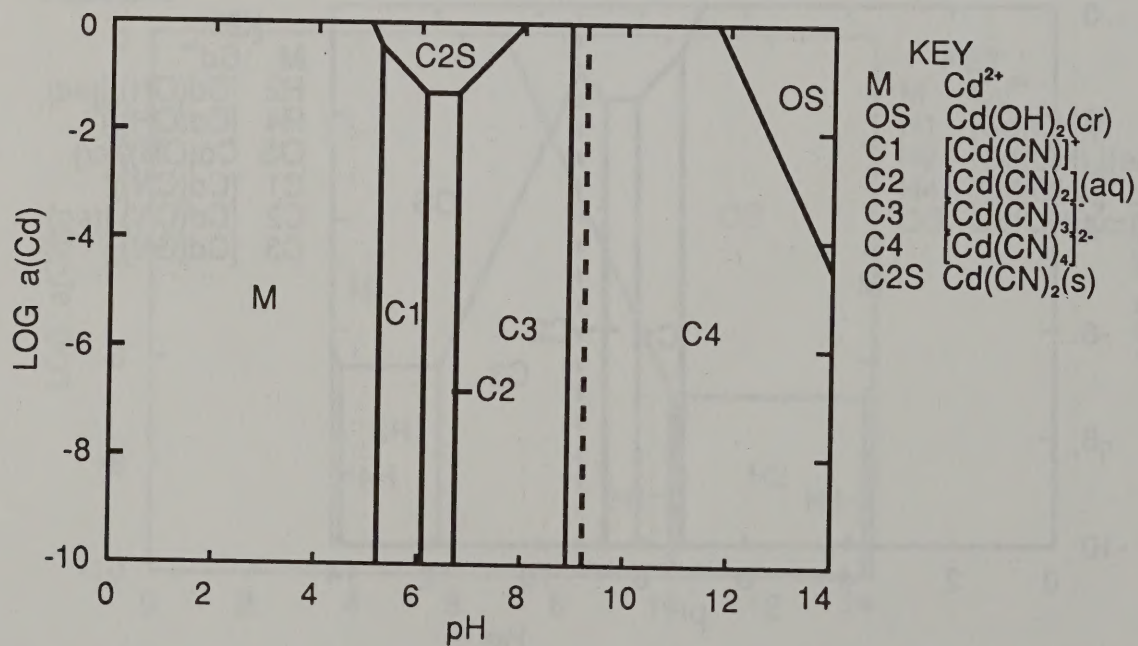


Figure E-35



*pCd-pH diagram for  $p\text{CN} = 3.0$ .*

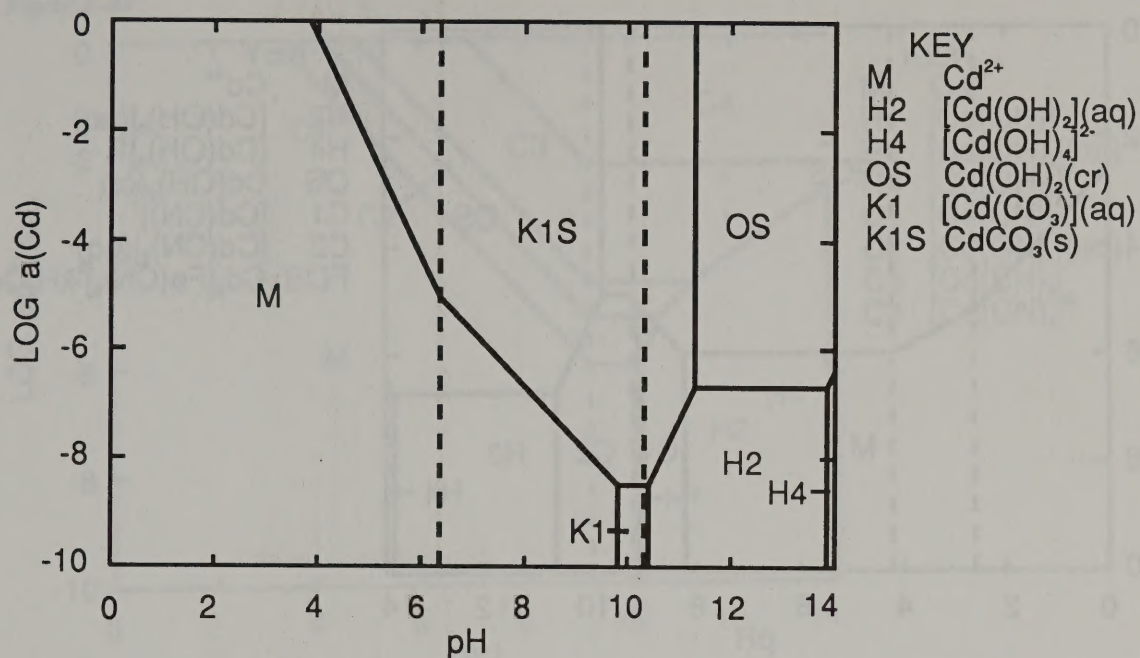
Figure E-36



*pCd-pH diagram for  $p\text{CN} = 2.0$ .*

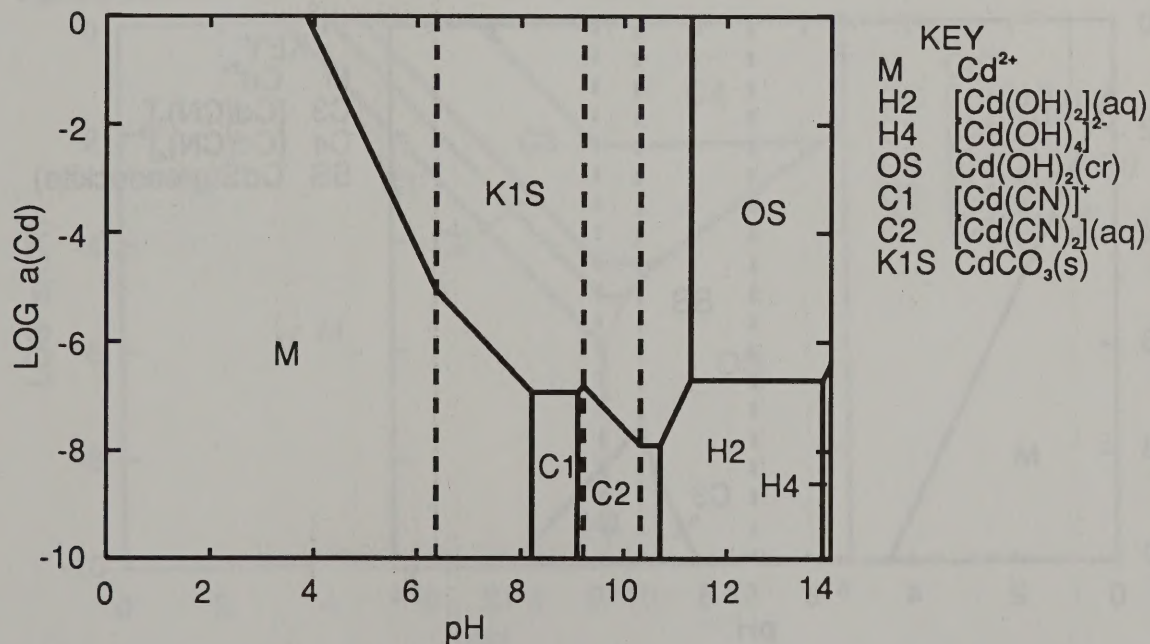


Figure E-37



*pCd-pH diagram for  $p\text{CO}_3 = 3.0$ .*

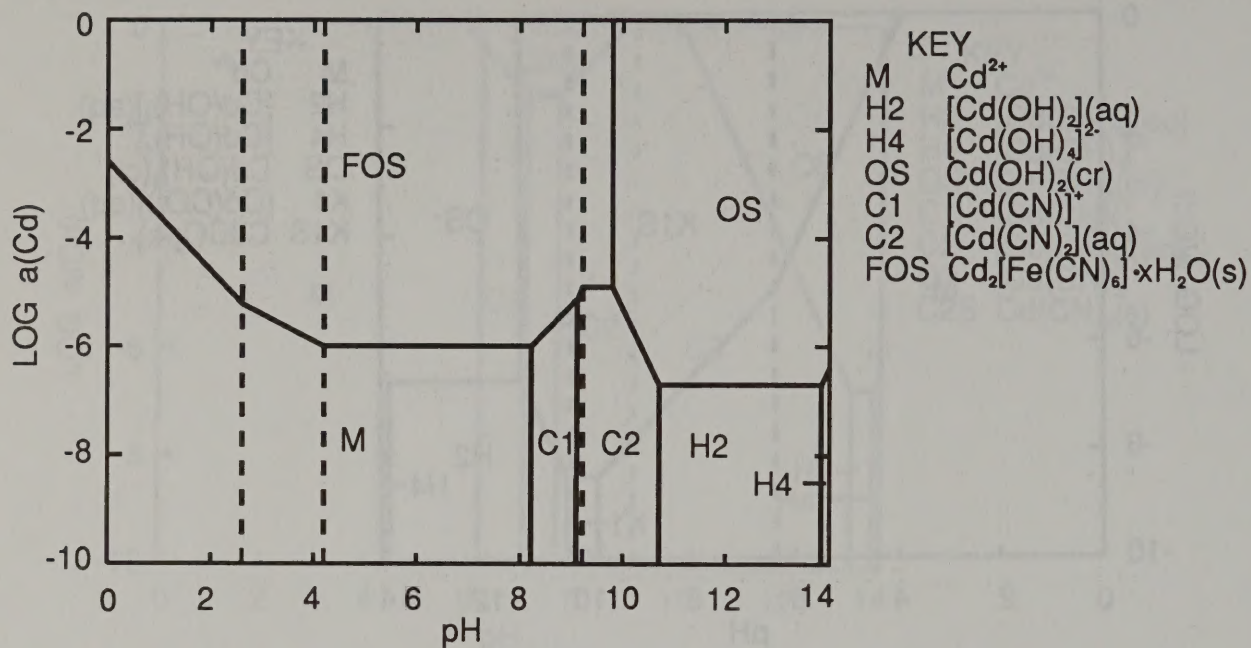
Figure E-38



*pCd-pH diagram for  $p\text{CN} = 5.0$  and  $p\text{CO}_3 = 3.0$ .*

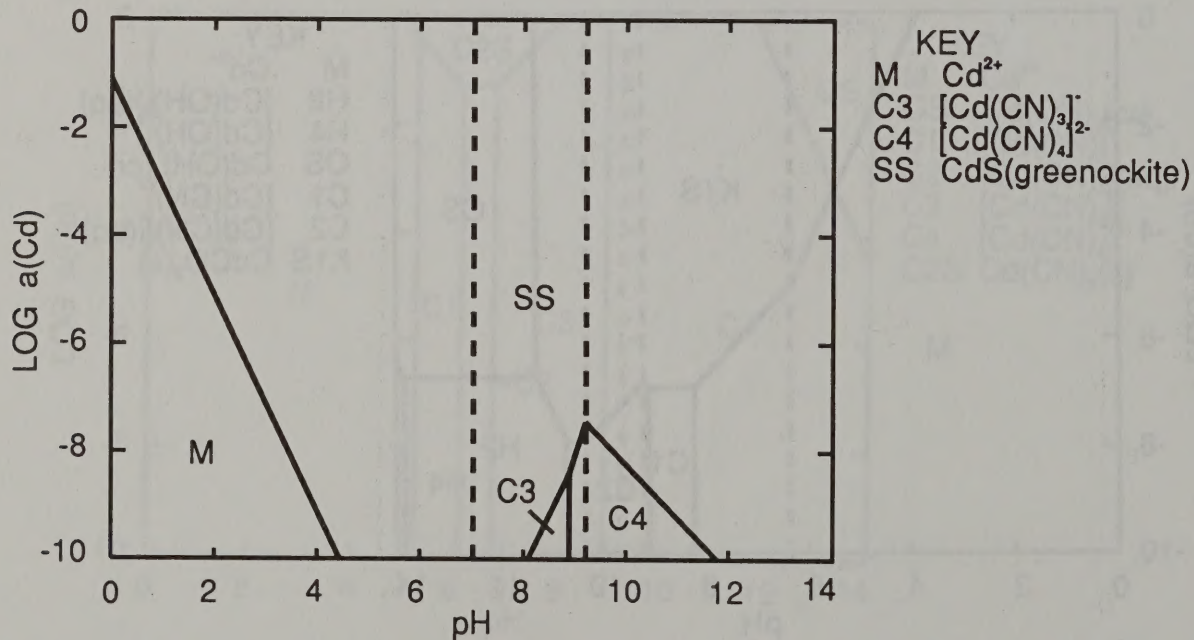


Figure E-39



$p\text{Cd}$ - $p\text{H}$  diagram for  $p\text{CN} = 5.0$  and  $p[\text{Fe}(\text{CN})_6^{4-}] = 4.0$ .

Figure E-40



$p\text{Cd}$ - $p\text{H}$  diagram for  $p\text{CN} = 2.0$  and  $p\text{SH} = 6.0$ .



Figure E-41

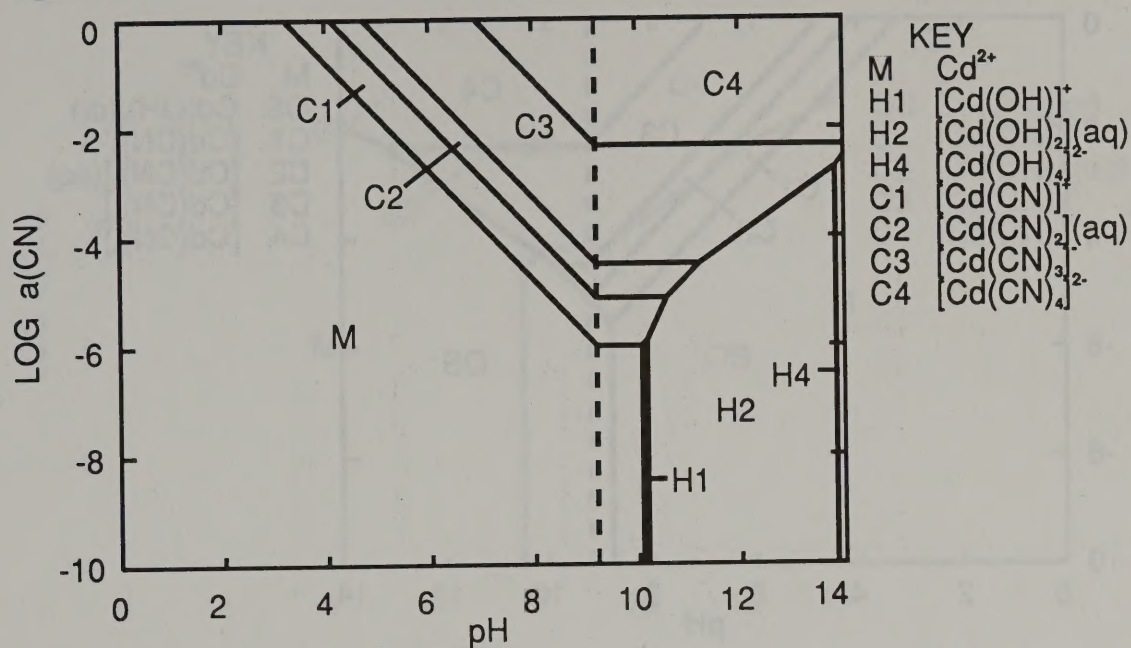
*pCN-pH diagram for cadmium solution species.*

Figure E-42

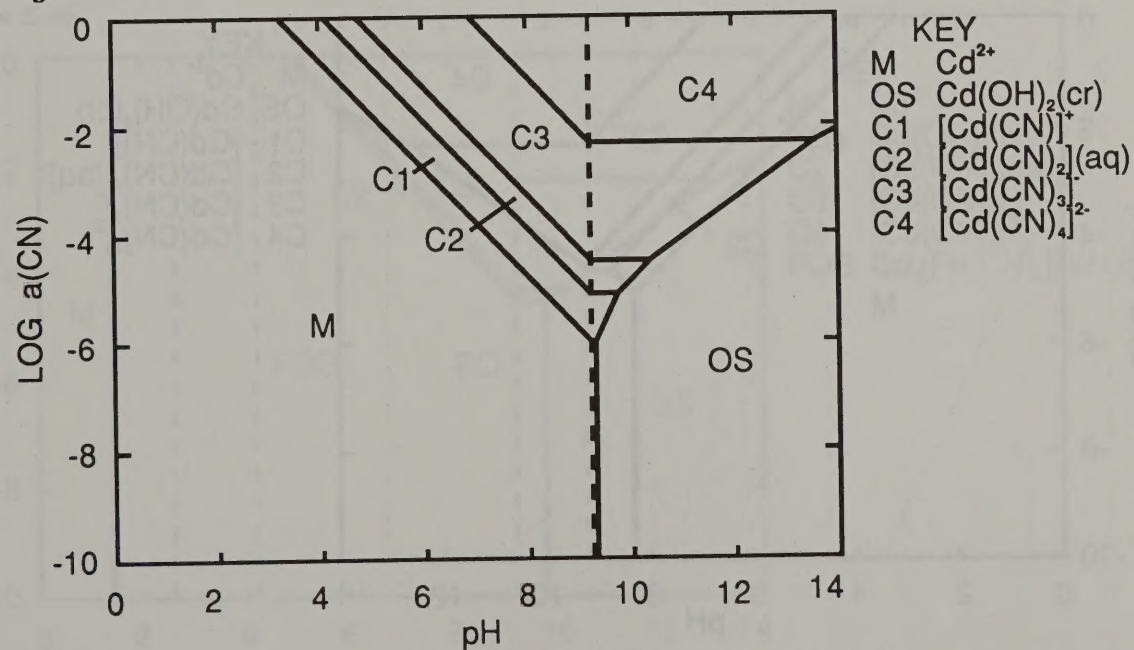
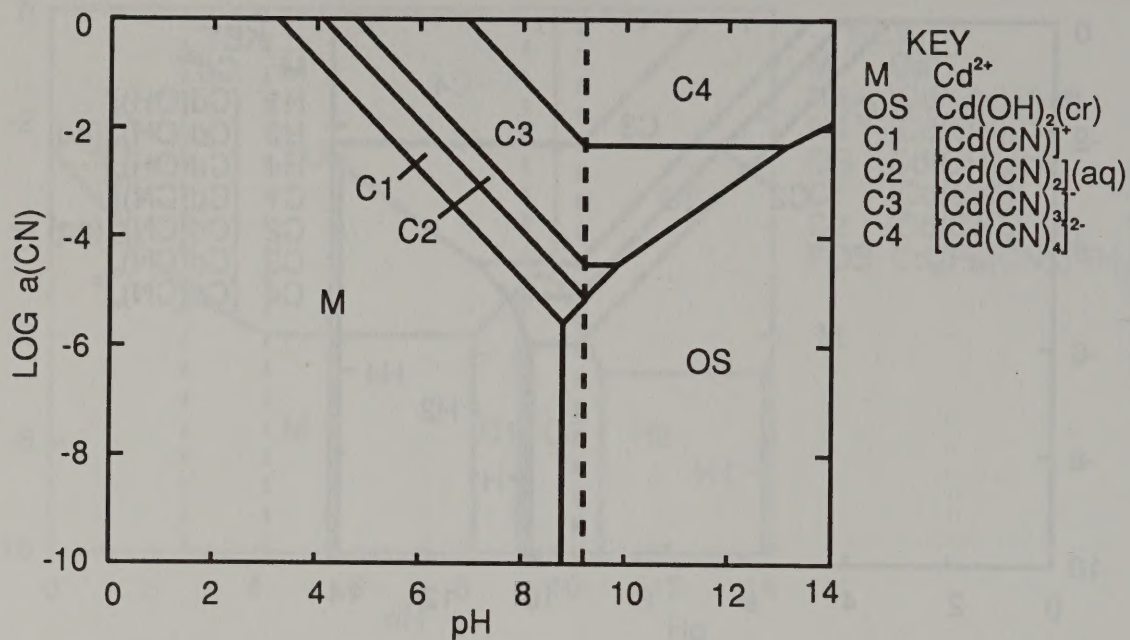
*pCN-pH diagram for  $p\text{Cd} = 5.0$ .*

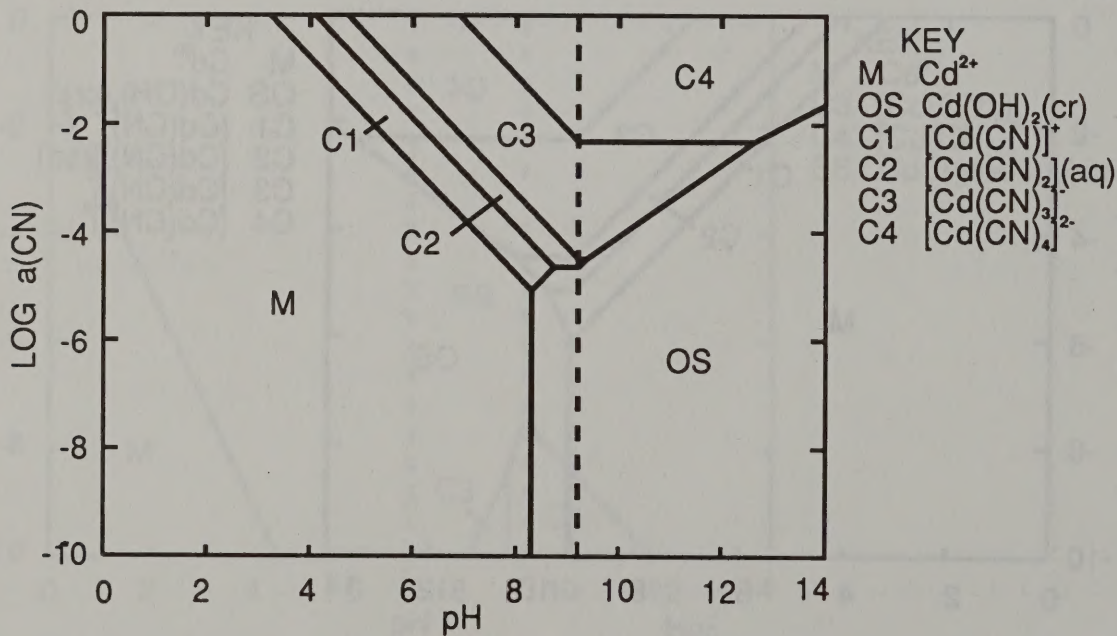


Figure E-43



*pCN-pH diagram for  $p\text{Cd} = 4.0$ .*

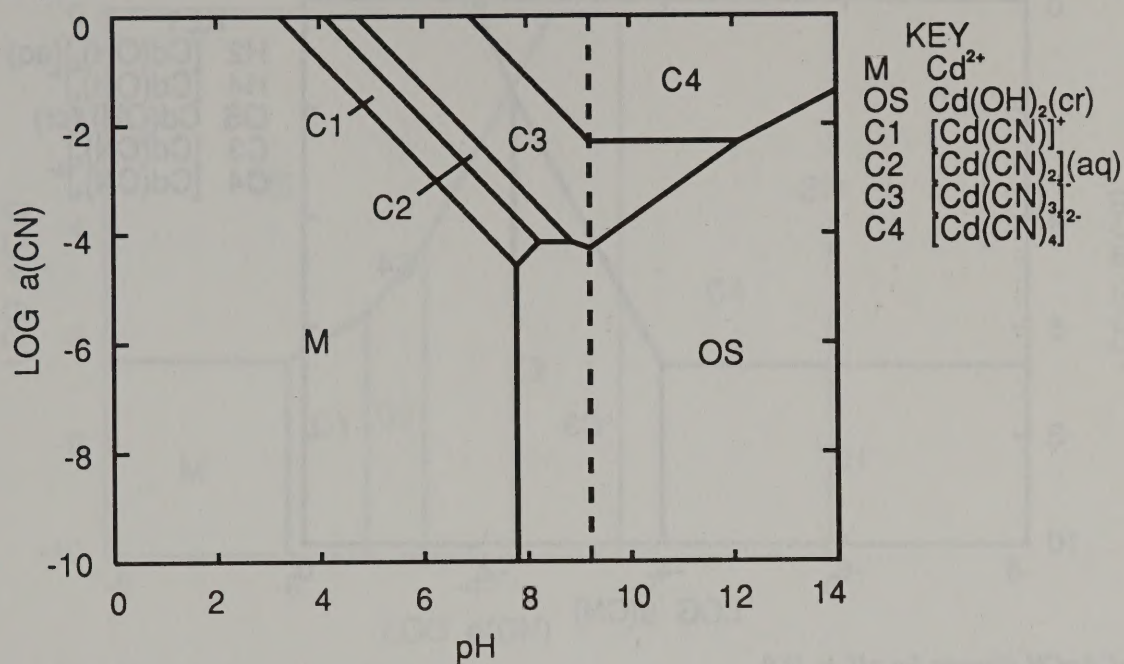
Figure E-44



*pCN-pH diagram for  $p\text{Cd} = 3.0$ .*

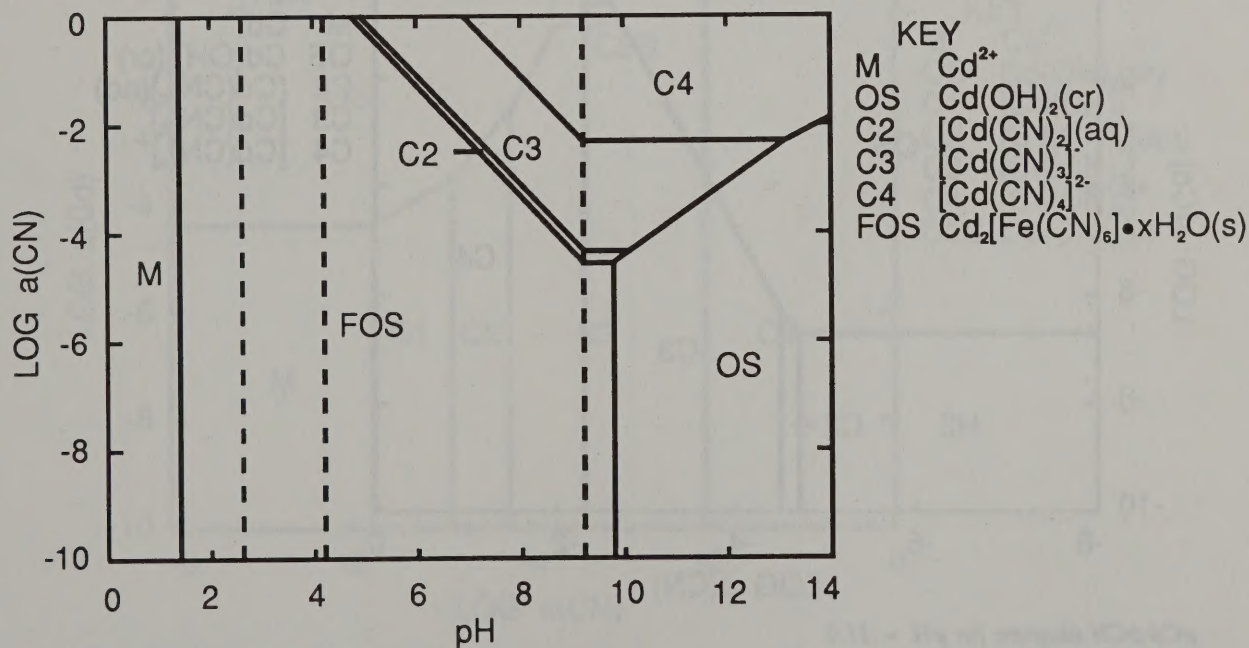


Figure E-45



*pCN-pH diagram for  $p\text{Cd} = 2.0$ .*

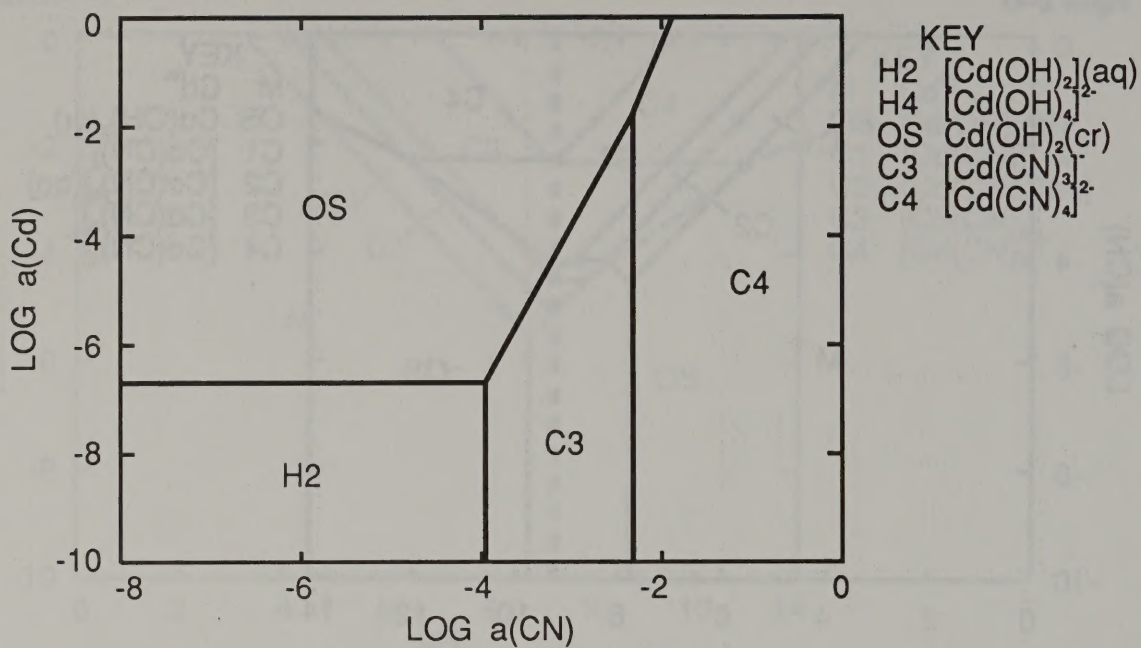
Figure E-46



*pCN-pH diagram for  $p\text{Cd} = 4.0$  and  $p[\text{Fe}(\text{CN})_6]^{4-} = 4.0$ .*

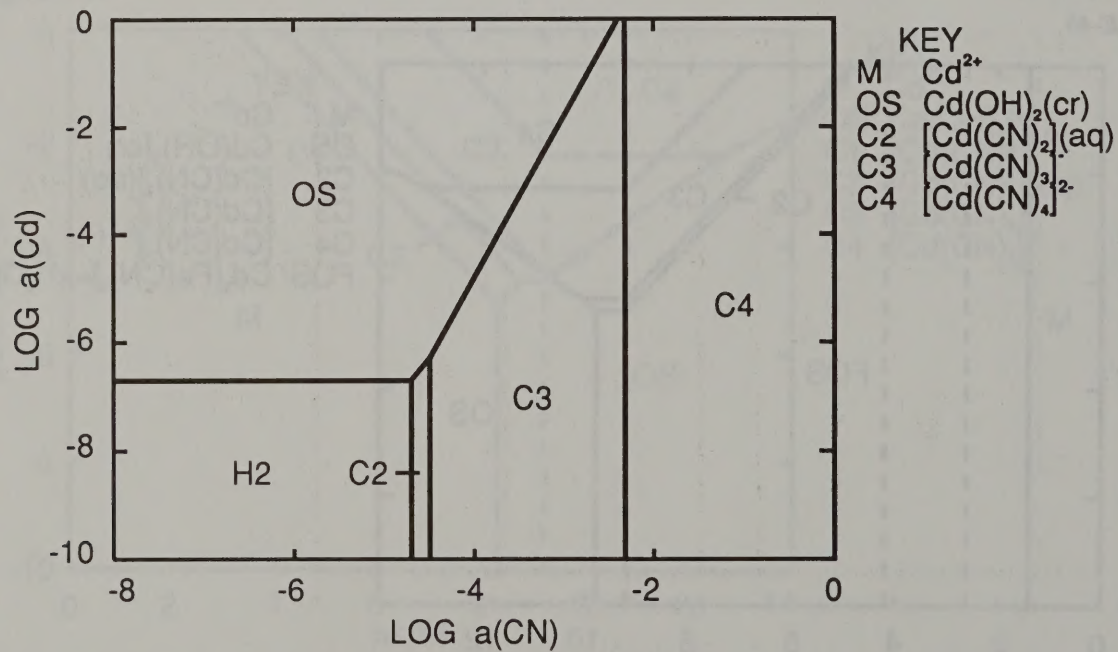


Figure E-47



*pCd-pCN diagram for pH = 12.0.*

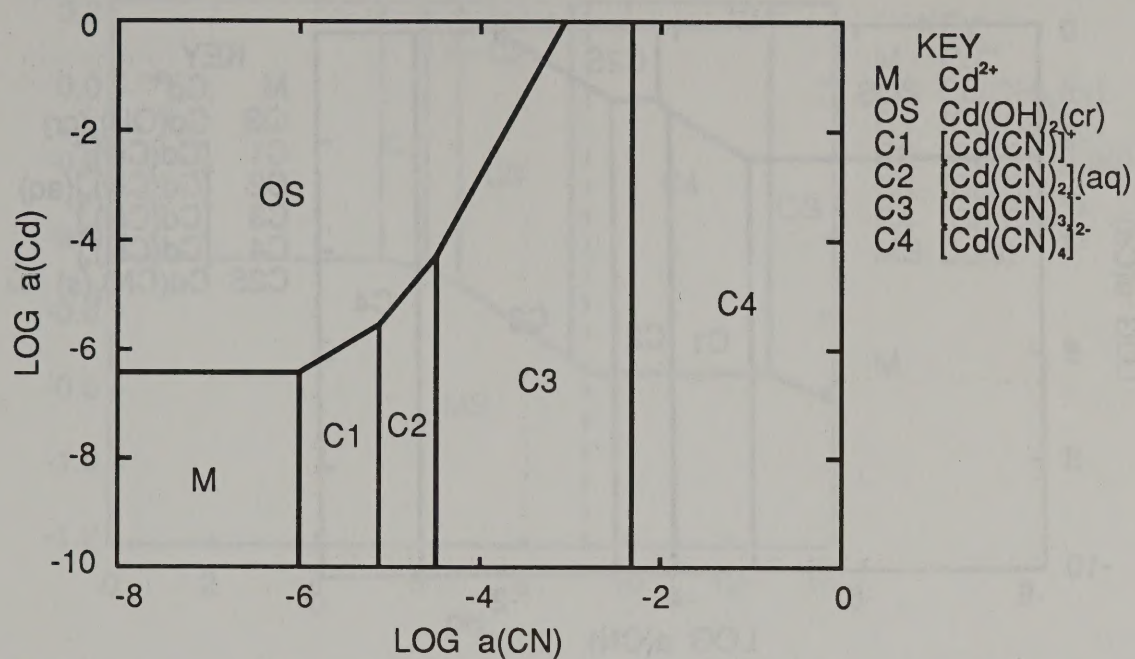
Figure E-48



*pCd-pCN diagram for pH = 11.0.*

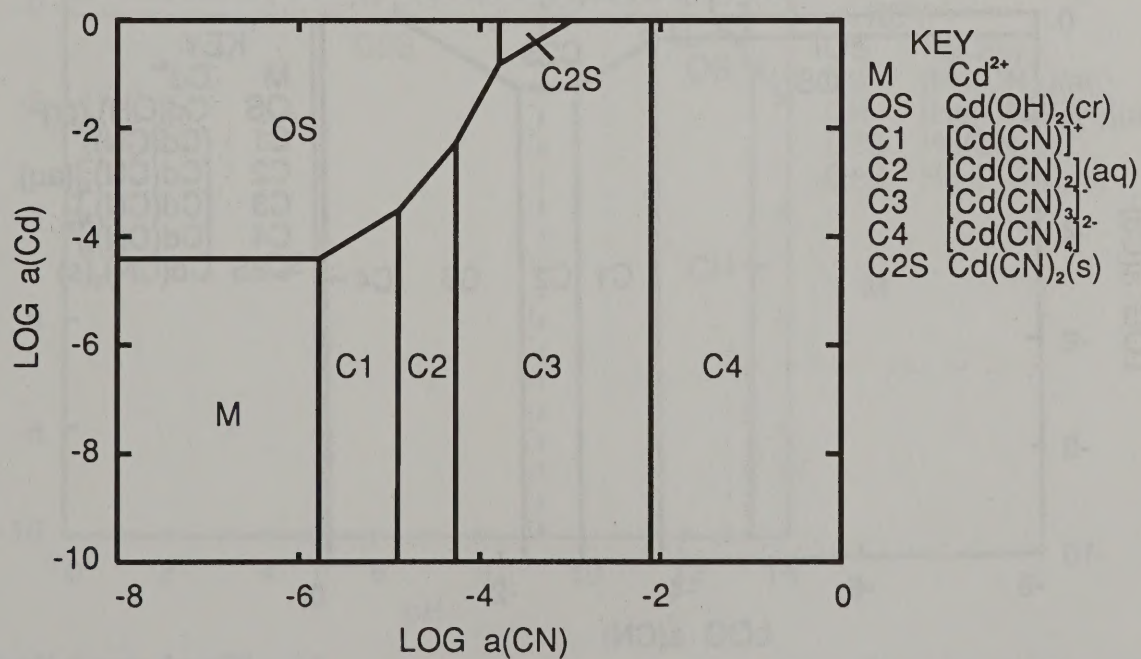


Figure E-49



*pCd-pCN diagram for pH = 10.0.*

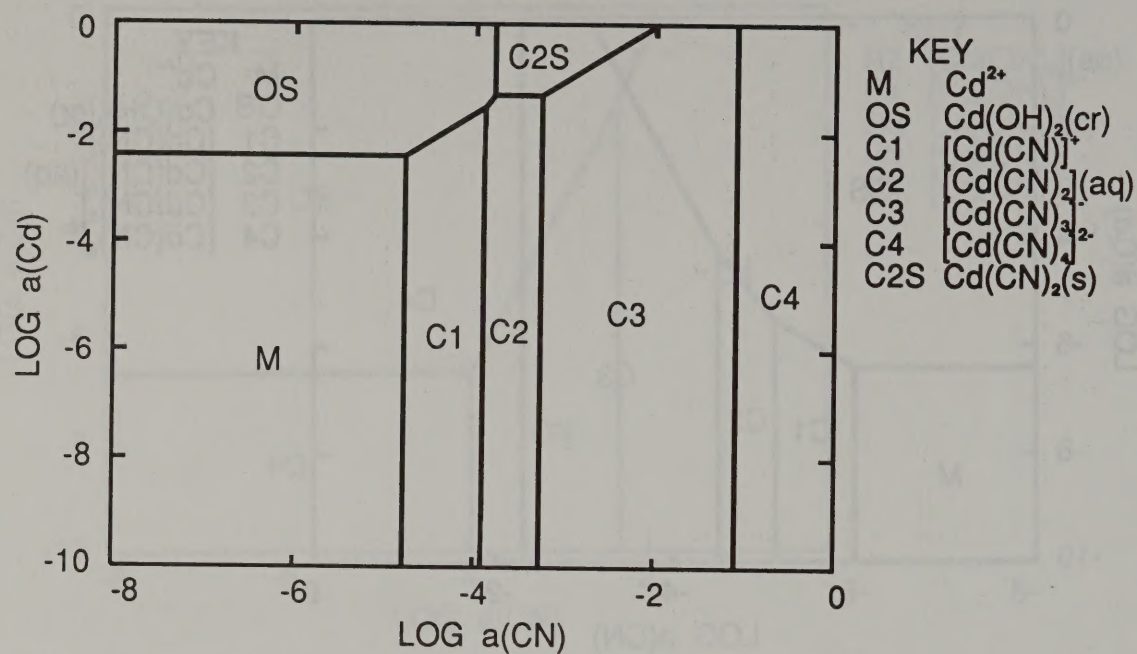
Figure E-50



*pCd-pCN diagram for pH = 9.0.*

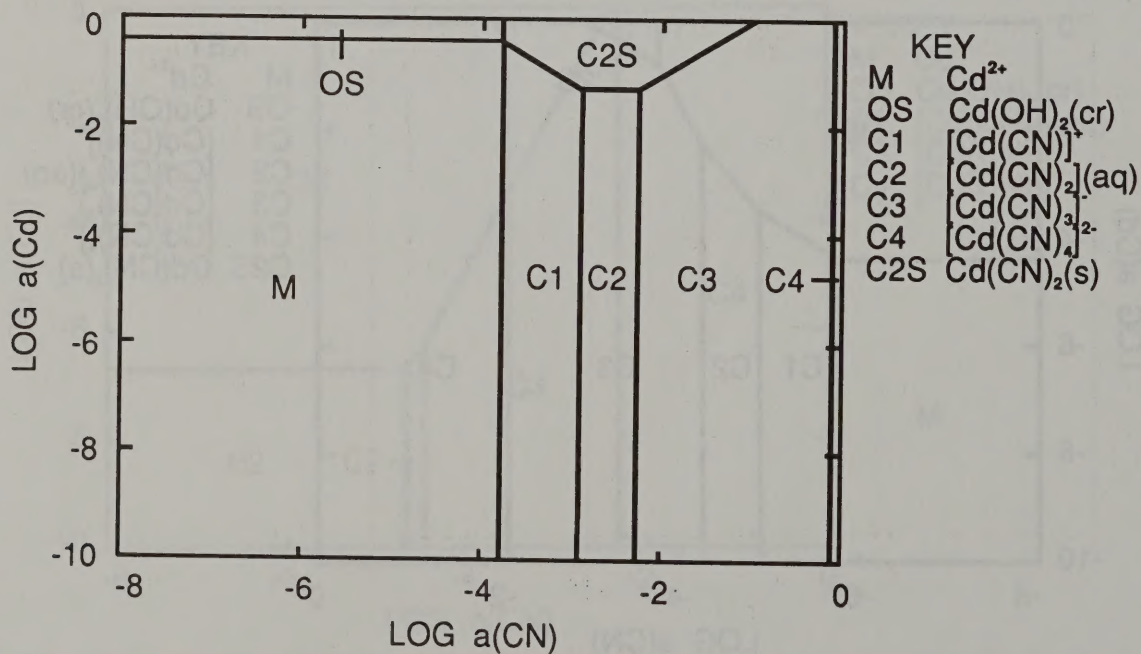


Figure E-51



$p\text{Cd}$ - $p\text{CN}$  diagram for  $\text{pH} = 8.0$ .

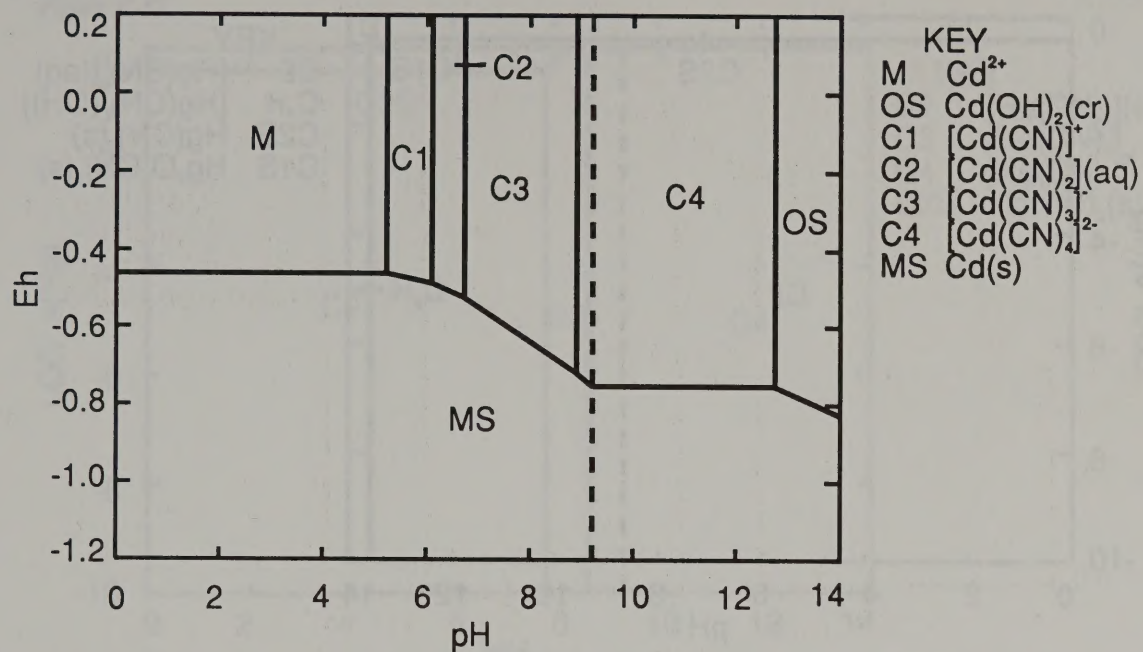
Figure E-52



$p\text{Cd}$ - $p\text{CN}$  diagram for  $\text{pH} = 7.0$ .

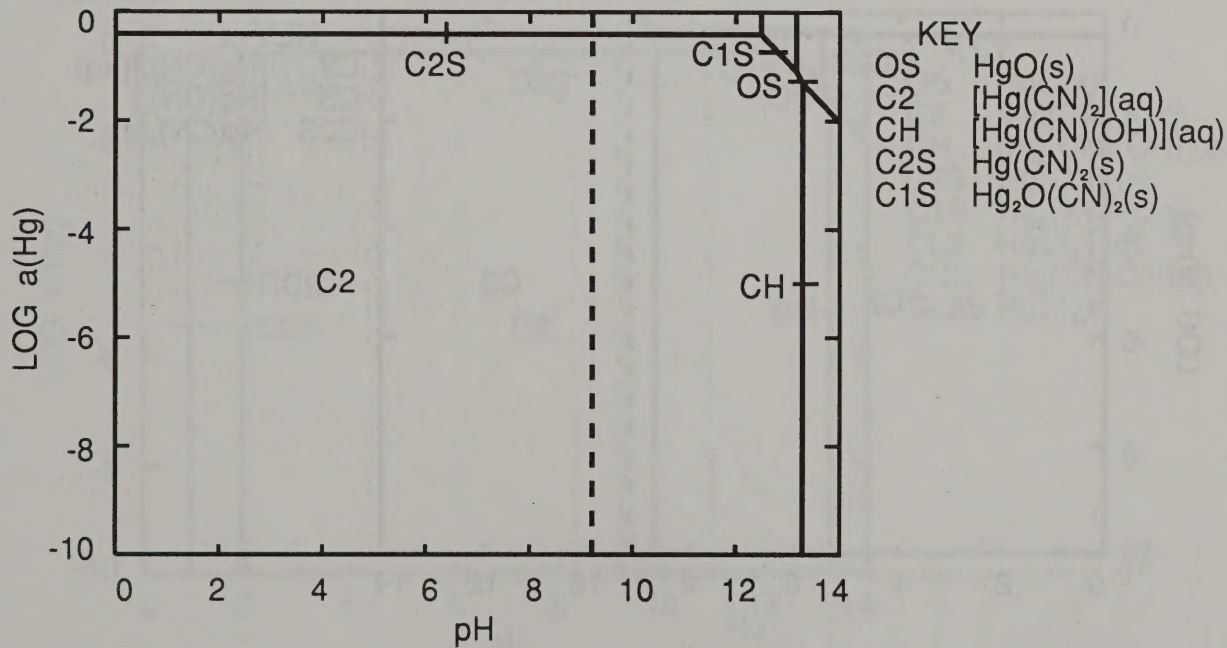


Figure E-53



*Eh-pH diagram for  $p\text{Cd} = 2.0$  and  $p\text{CN} = 2.0$ .*

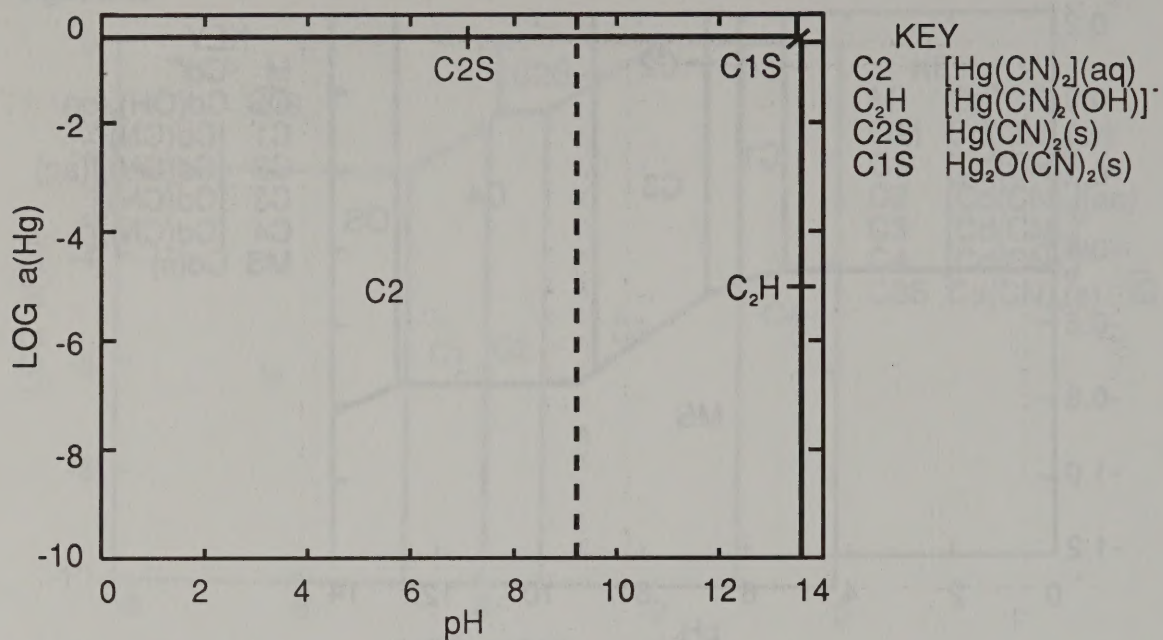
Figure E-54



*pHg-pH diagram for  $p\text{CN} = 5.0$ .*

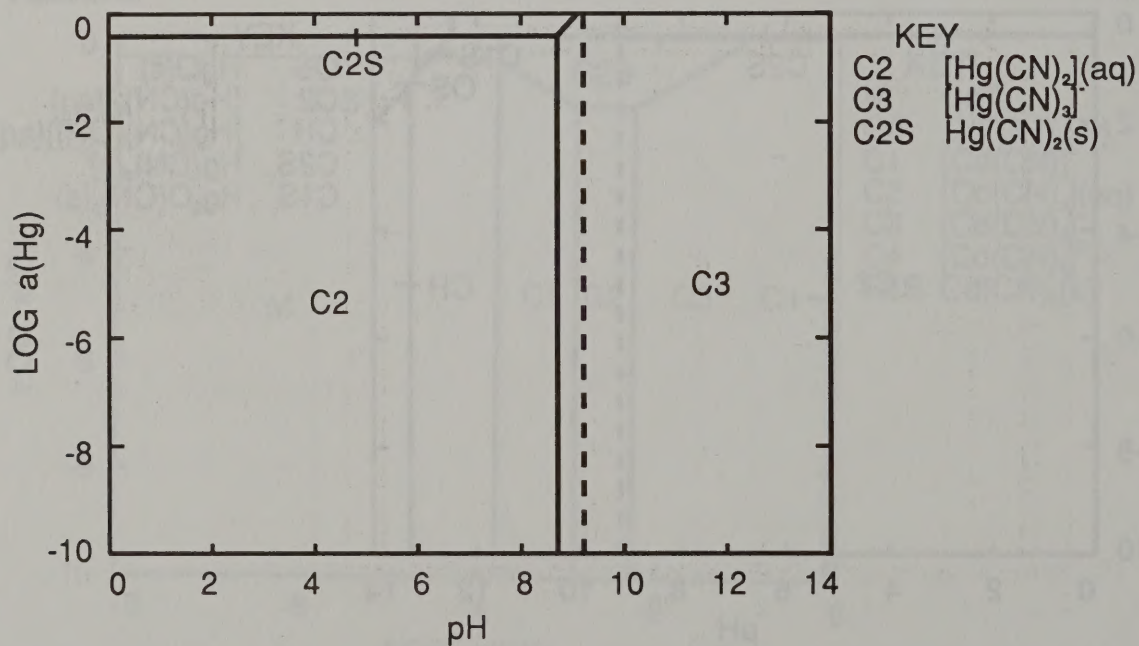


Figure E-55



*pHg-pH diagram for  $p\text{CN} = 4.0$ .*

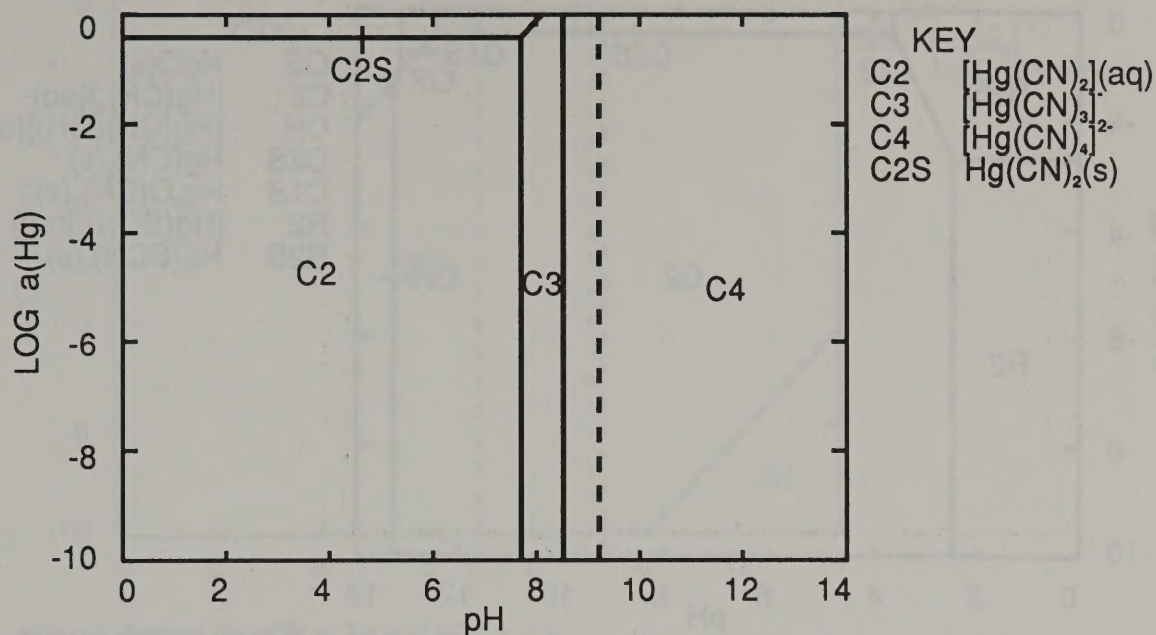
Figure E-56



*pHg-pH diagram for  $p\text{CN} = 3.0$ .*

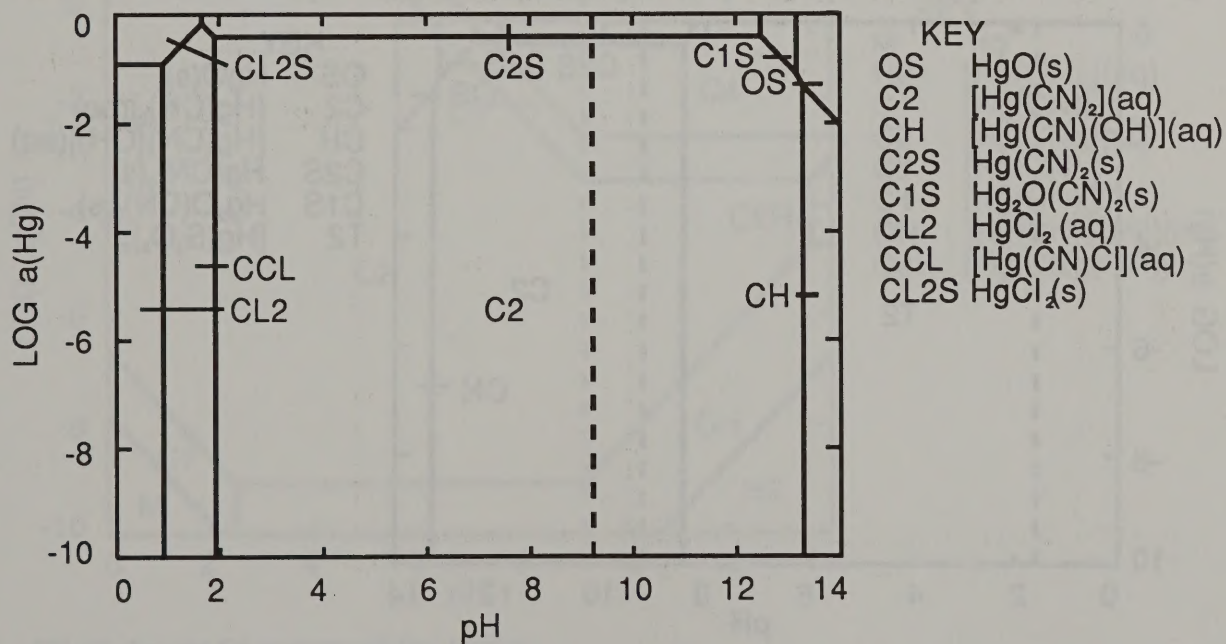


Figure E-57



*pHg-pH diagram for  $p\text{CN} = 2.0$ .*

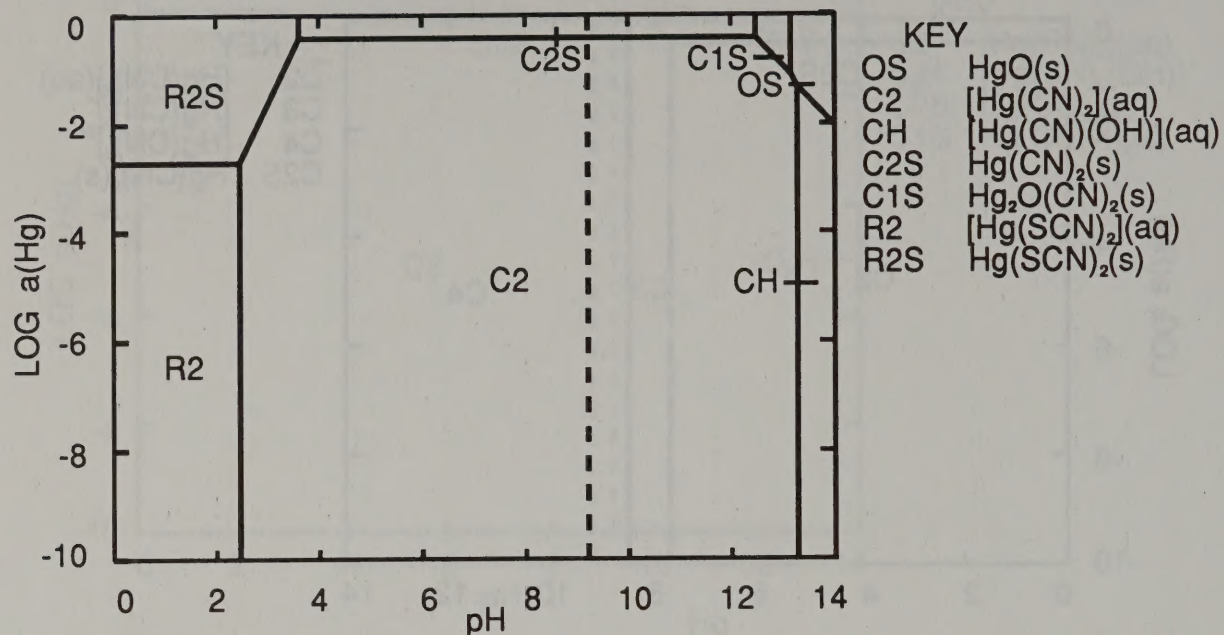
Figure E-58



*pHg-pH diagram for  $p\text{CN} = 5.0$  and  $p\text{Cl} = 3.0$ .*

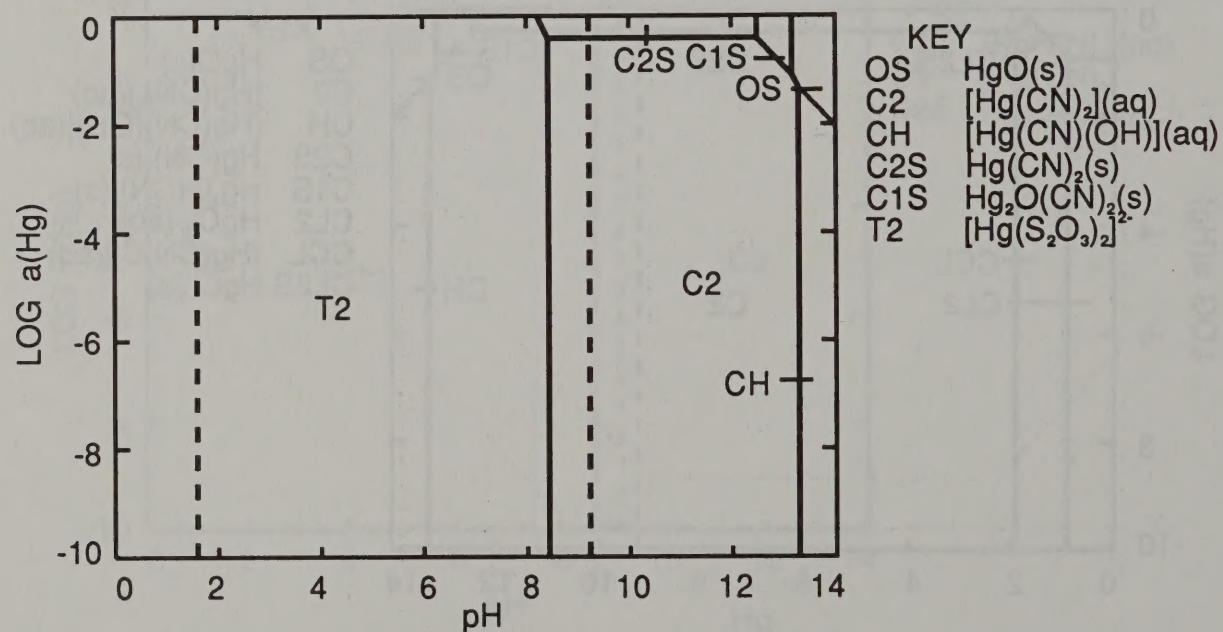


Figure E-59



*pHg-pH diagram for  $p\text{CN} = 5.0$  and  $p\text{SCN} = 4.0$ .*

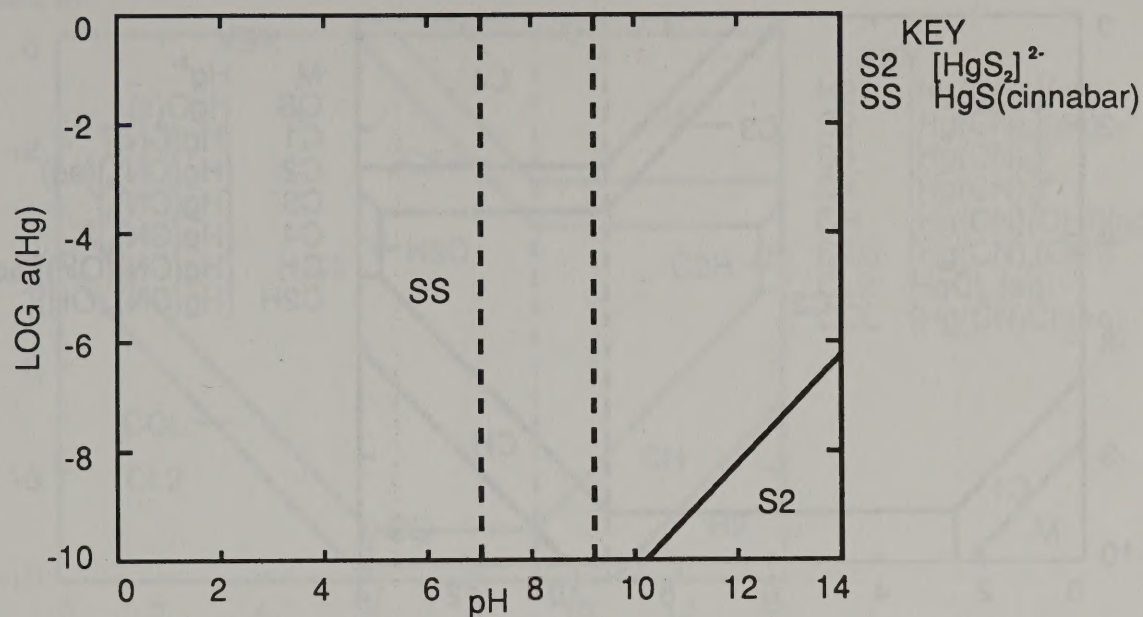
Figure E-60



*pHg-pH diagram for  $p\text{CN} = 5.0$  and  $p\text{S}_2\text{O}_3 = 4.0$ .*

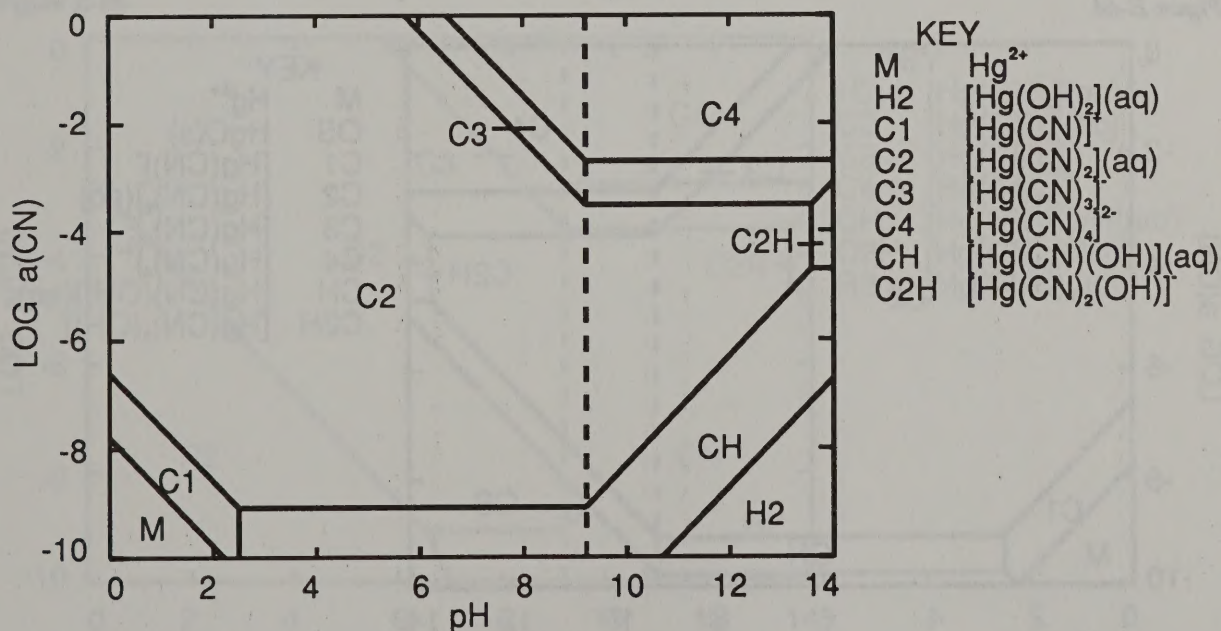


Figure E-61



*pHg-pH diagram for  $p\text{CN} = 2.0$  and  $p\text{SH} = 6.0$ .*

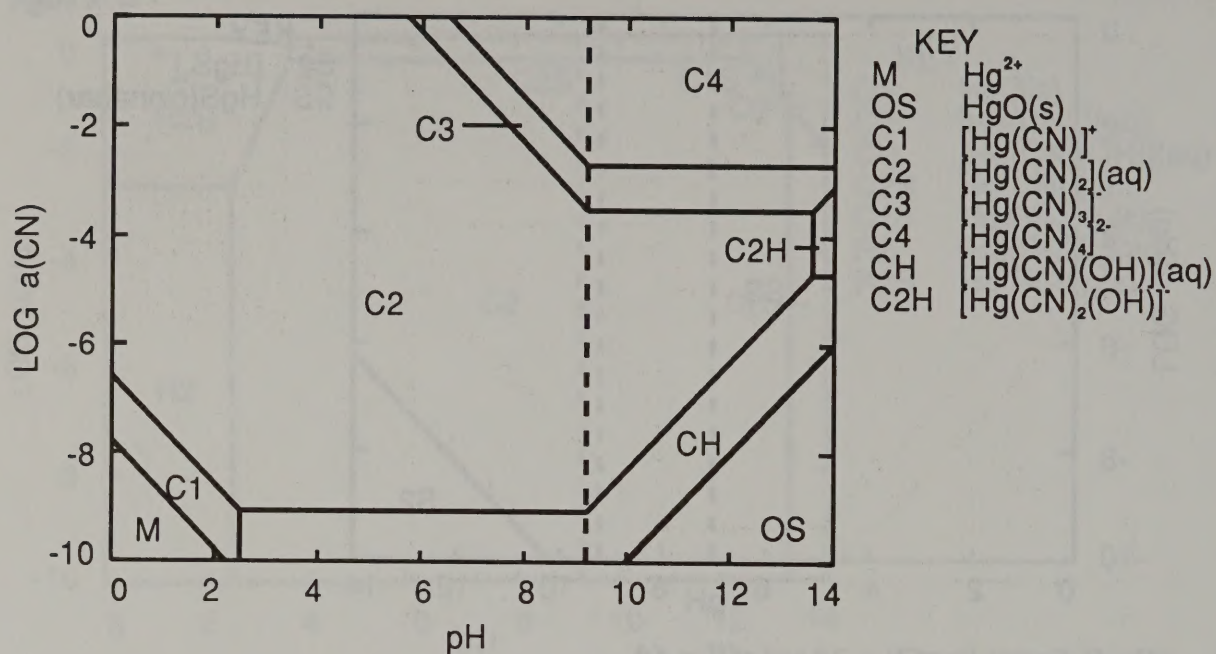
Figure E-62



*pCN-pH diagram for mercury solution species.*

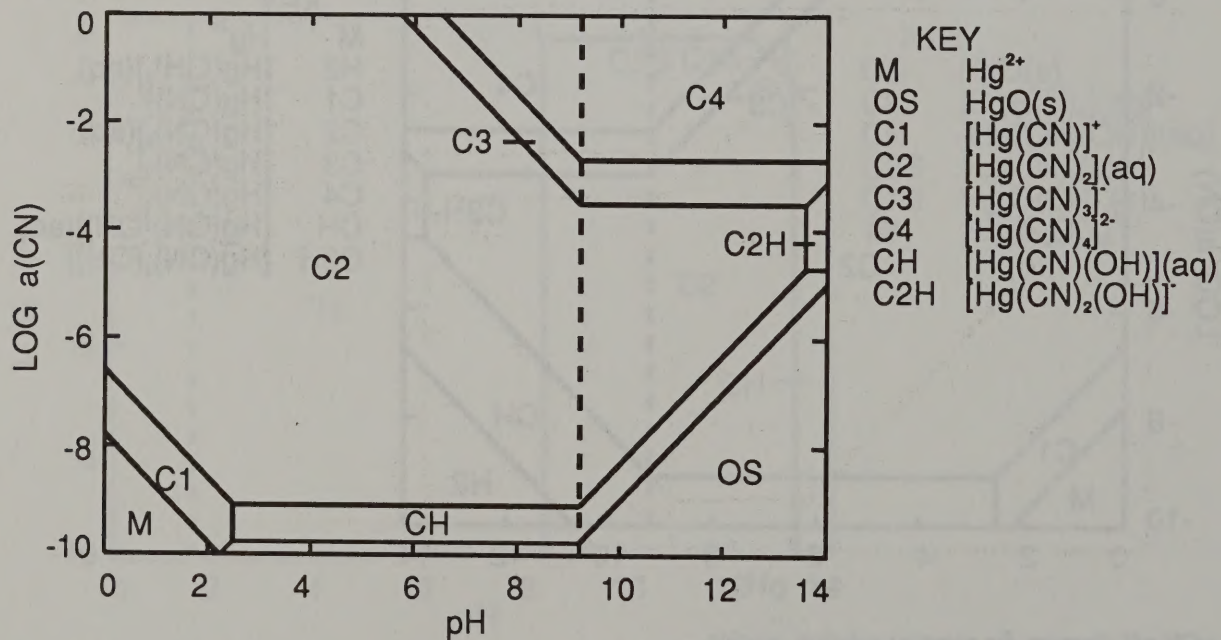


Figure E-63



*pCN-pH diagram for  $\text{pH}_{\text{Hg}} = 3.0$ .*

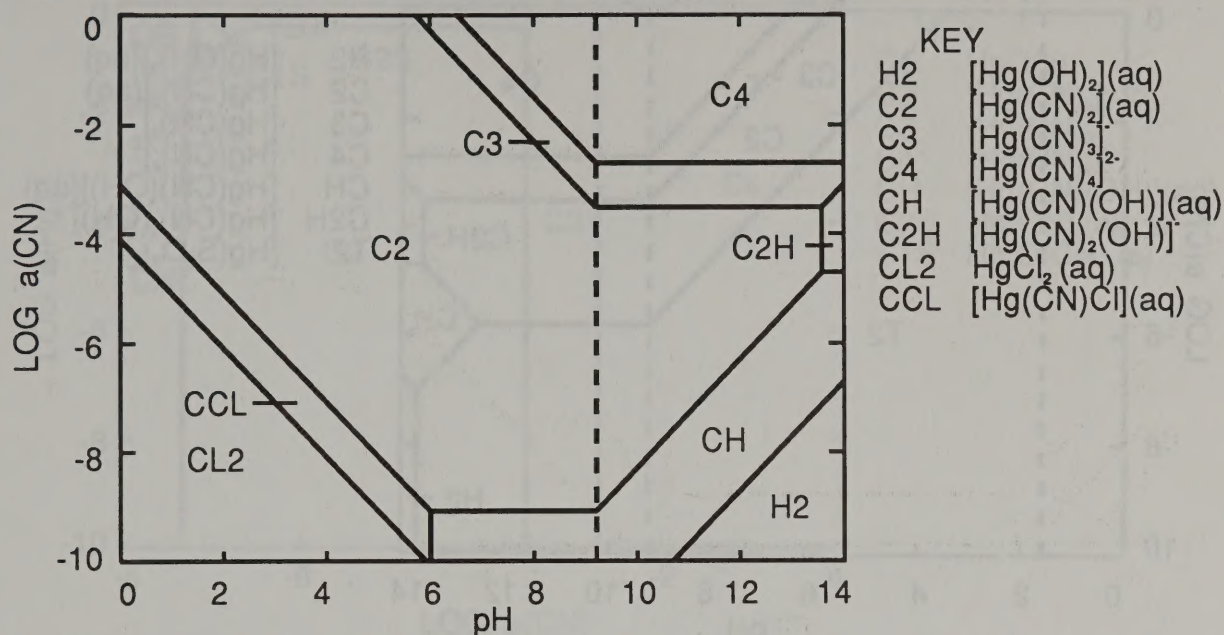
Figure E-64



*pCN-pH diagram for  $\text{pH}_{\text{Hg}} = 2.0$ .*

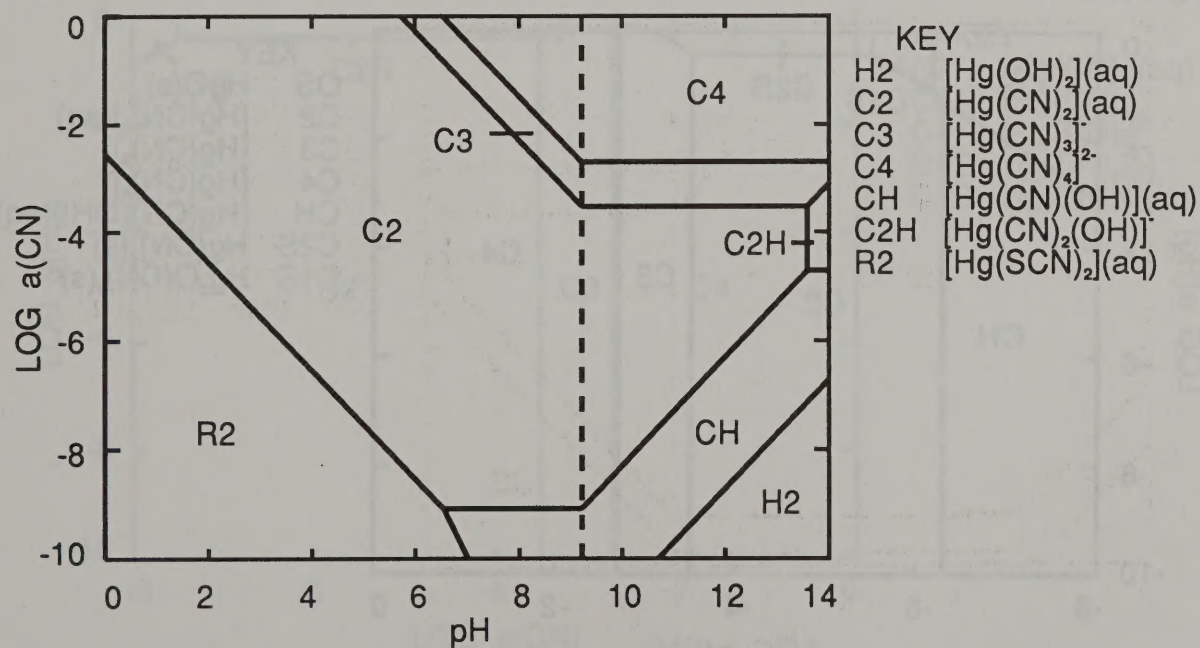


Figure E-65



*pCN-pH diagram for mercury solution species with  $p\text{Cl} = 3.0$ .*

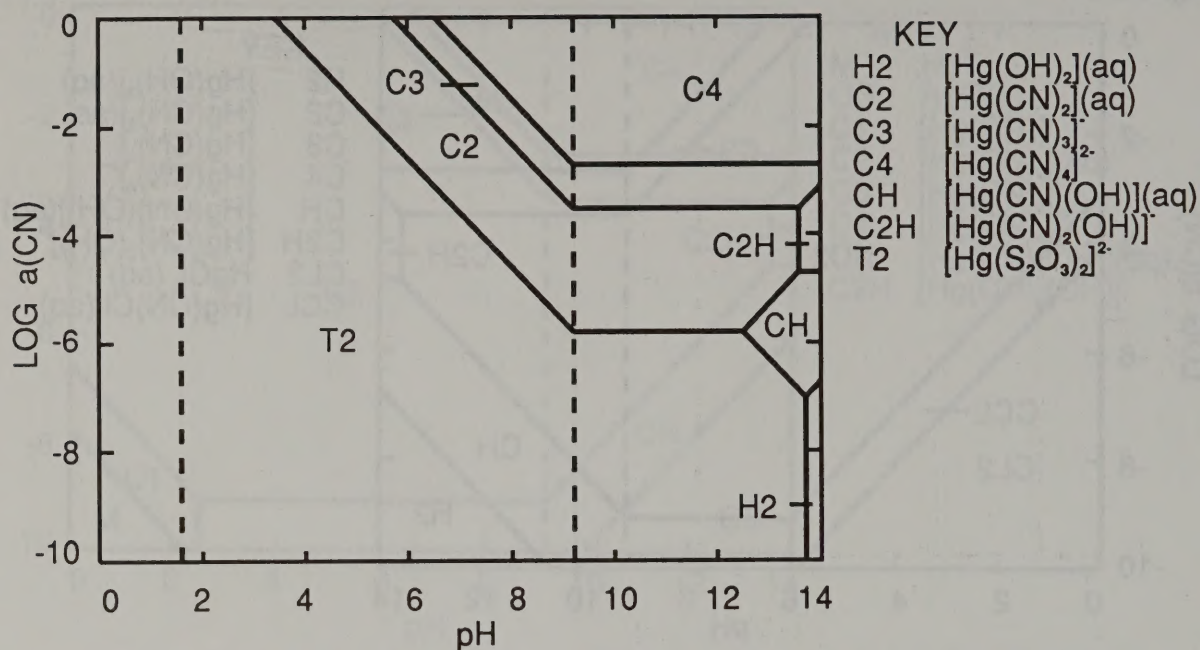
Figure E-66



*pCN-pH diagram for mercury solution species with  $p\text{SCN} = 4.0$ .*

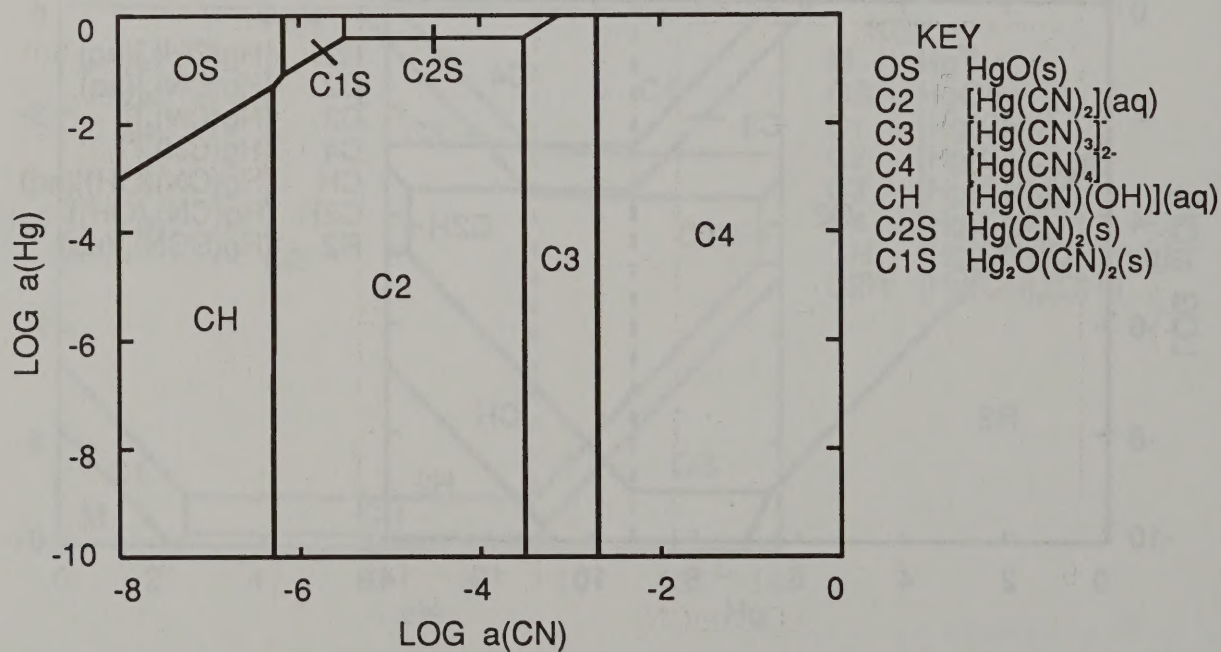


Figure E-67



*pCN-pH diagram for mercury solution species with  $p\text{S}_2\text{O}_3 = 4.0$ .*

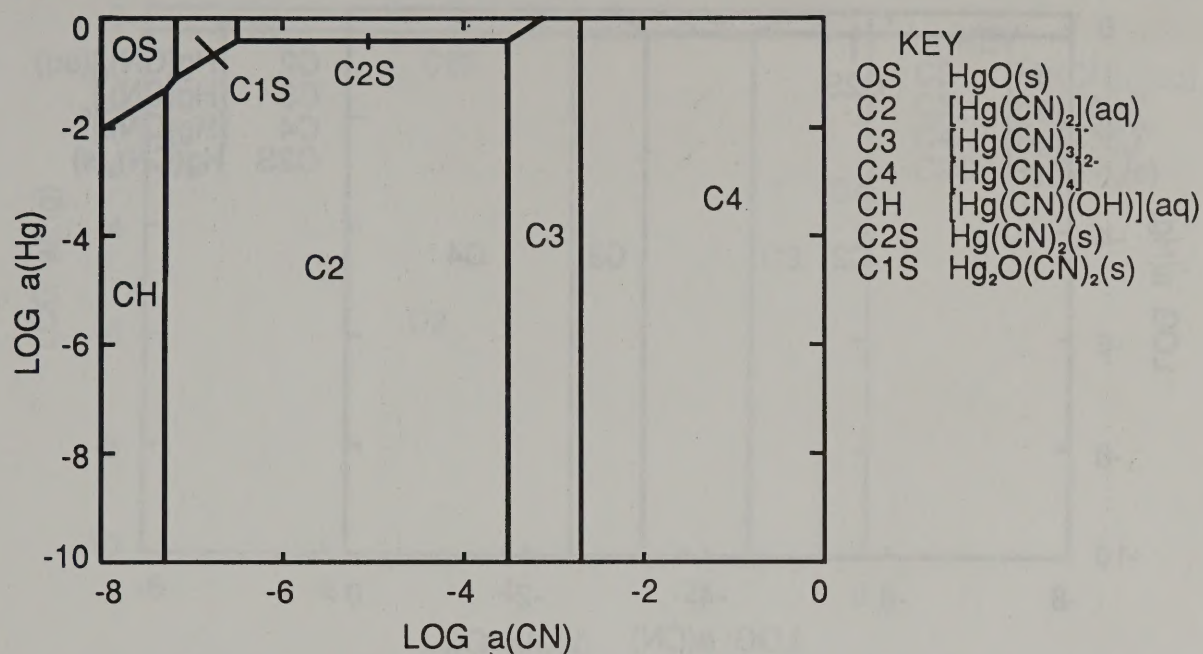
Figure E-68



*pHg-pCN diagram for  $\text{pH} = 12.0$ .*

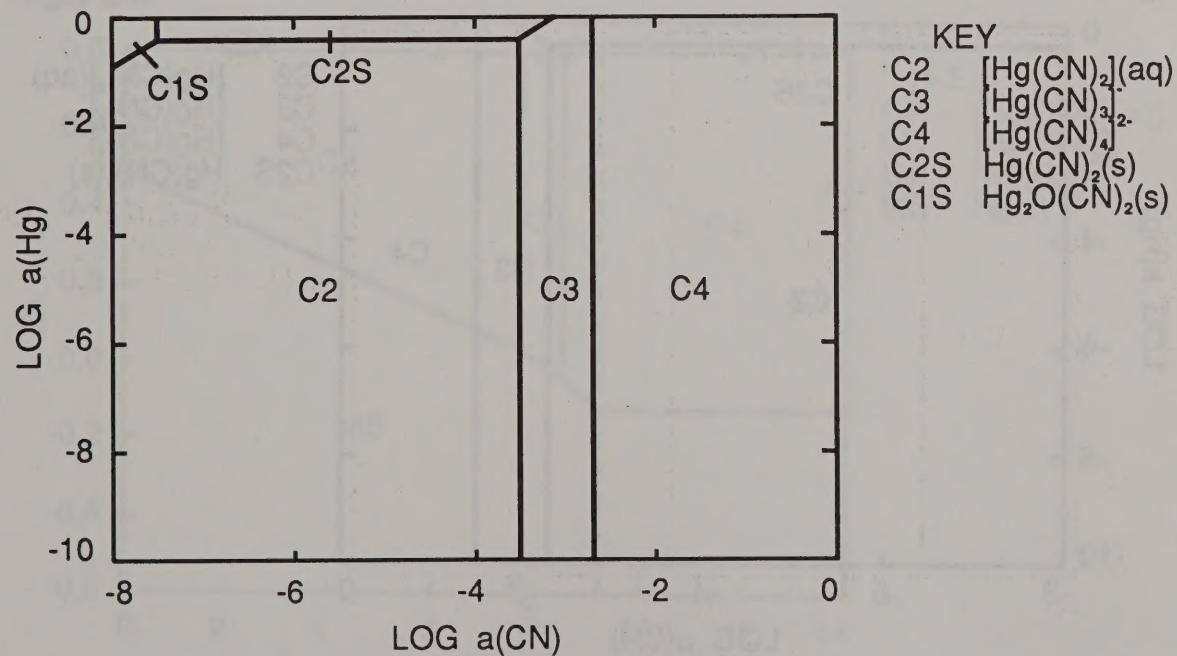


Figure E-69



*pHg-pCN diagram for pH = 11.0.*

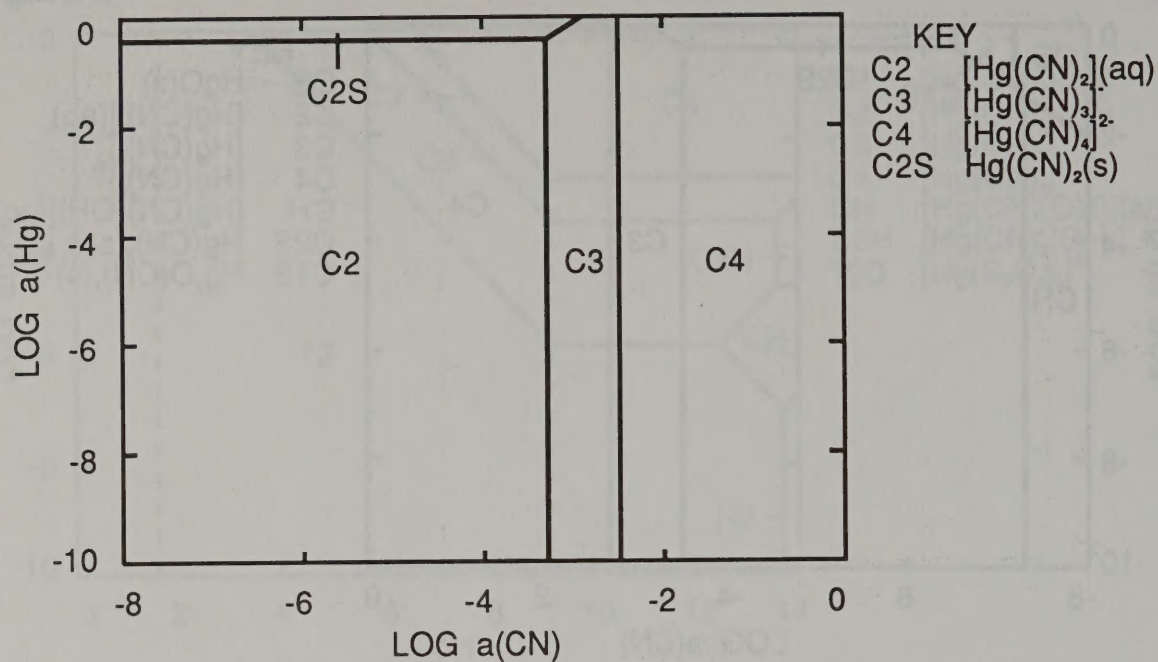
Figure E-70



*pHg-pCN diagram for pH = 10.0.*

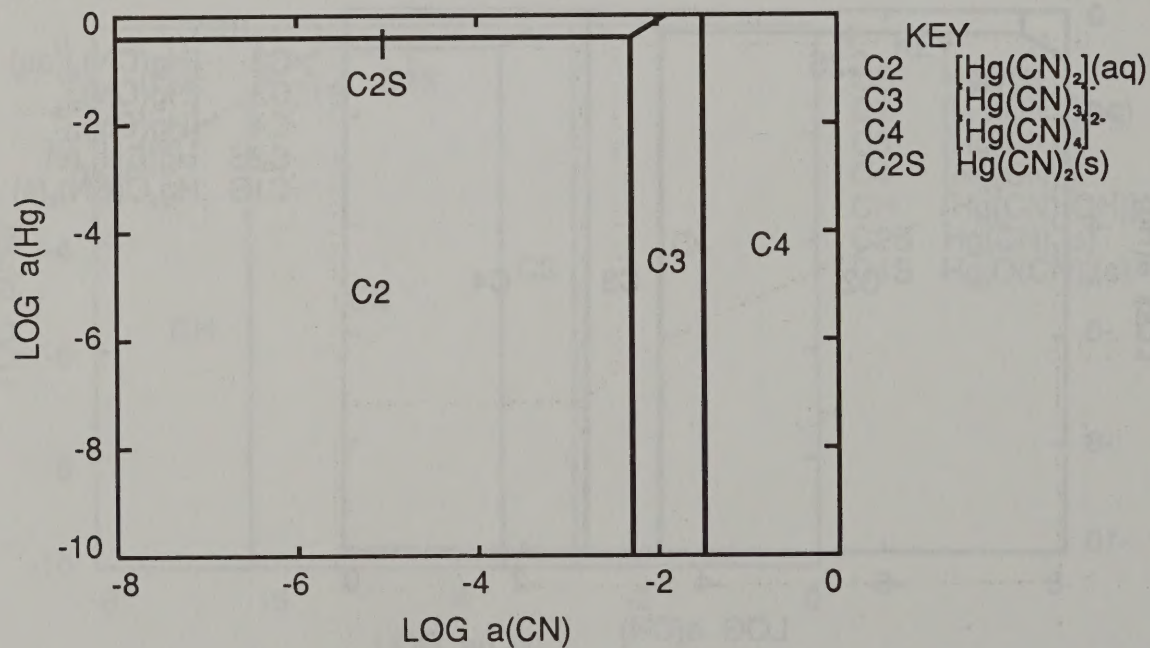


Figure E-71



*pHg-pCN diagram for  $\text{pH} = 9.0$ .*

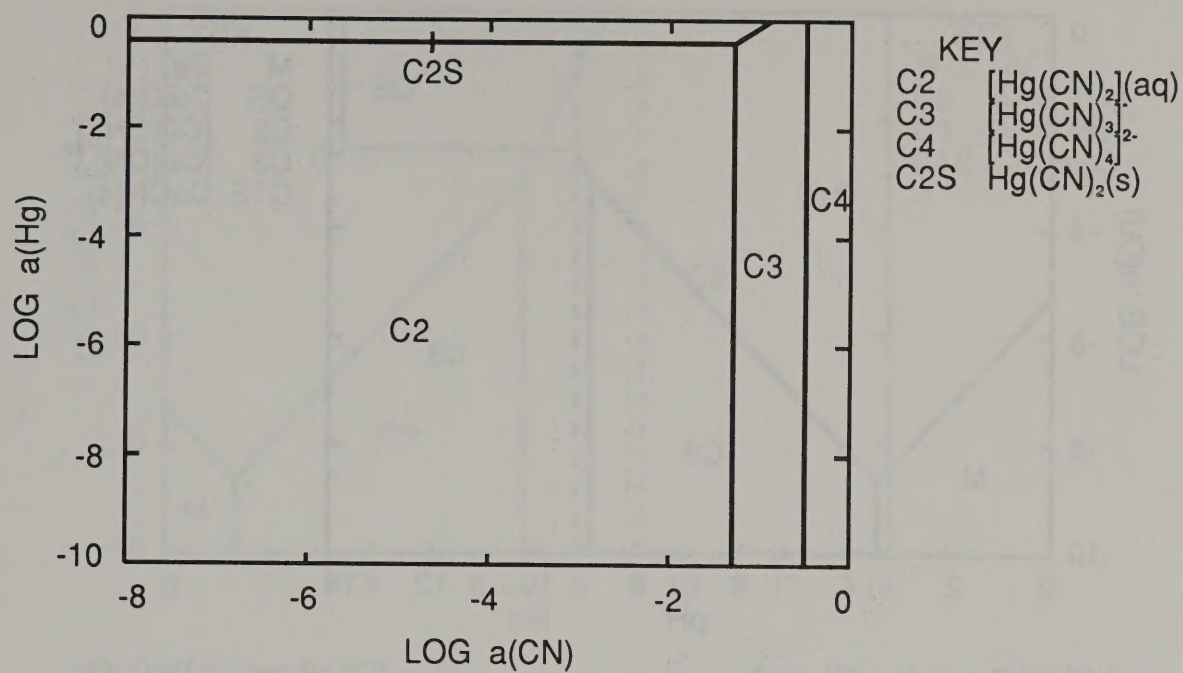
Figure E-72



*pHg-pCN diagram for  $\text{pH} = 8.0$ .*

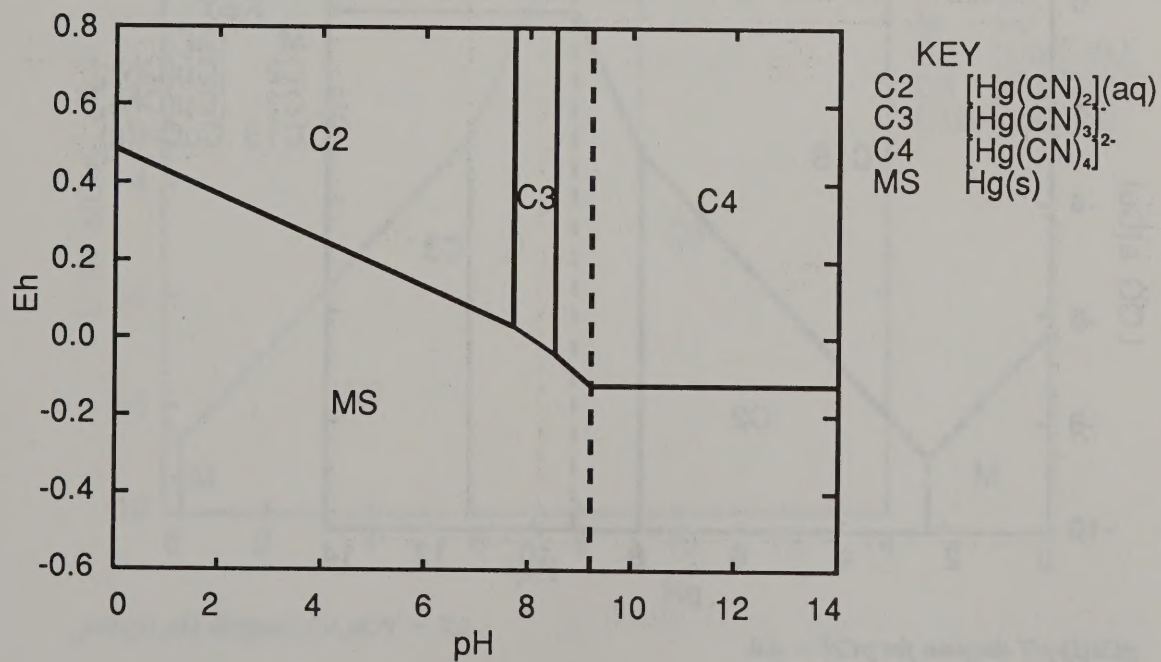


Figure E-73



*pHg-pCN diagram for pH = 7.0.*

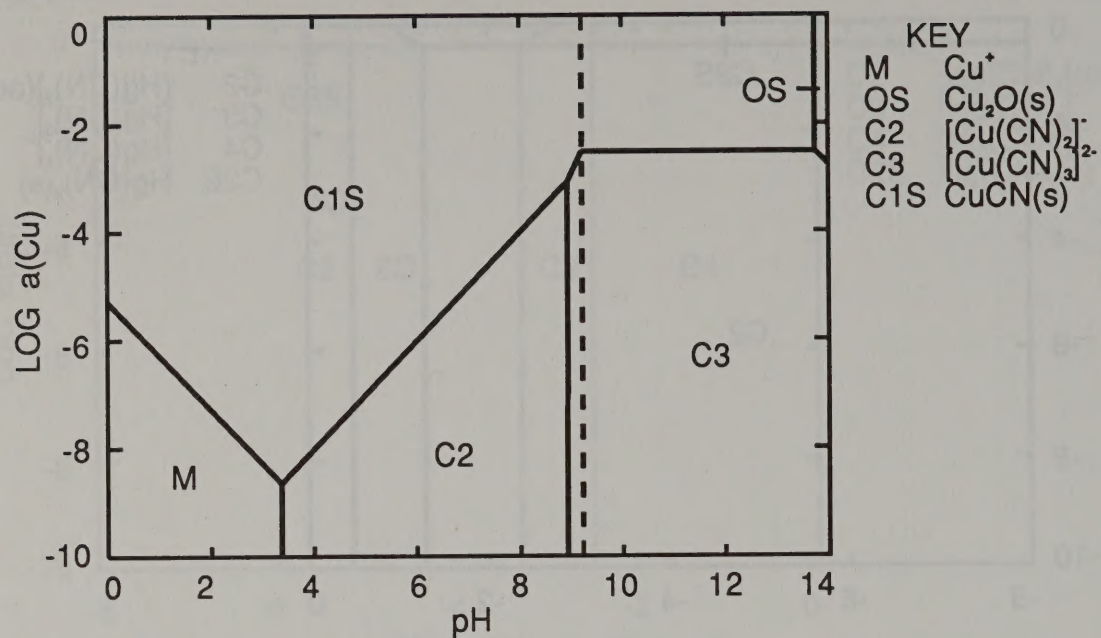
Figure E-74



*Eh-pH diagram for pHg = 2.0 and pCN = 2.0.*

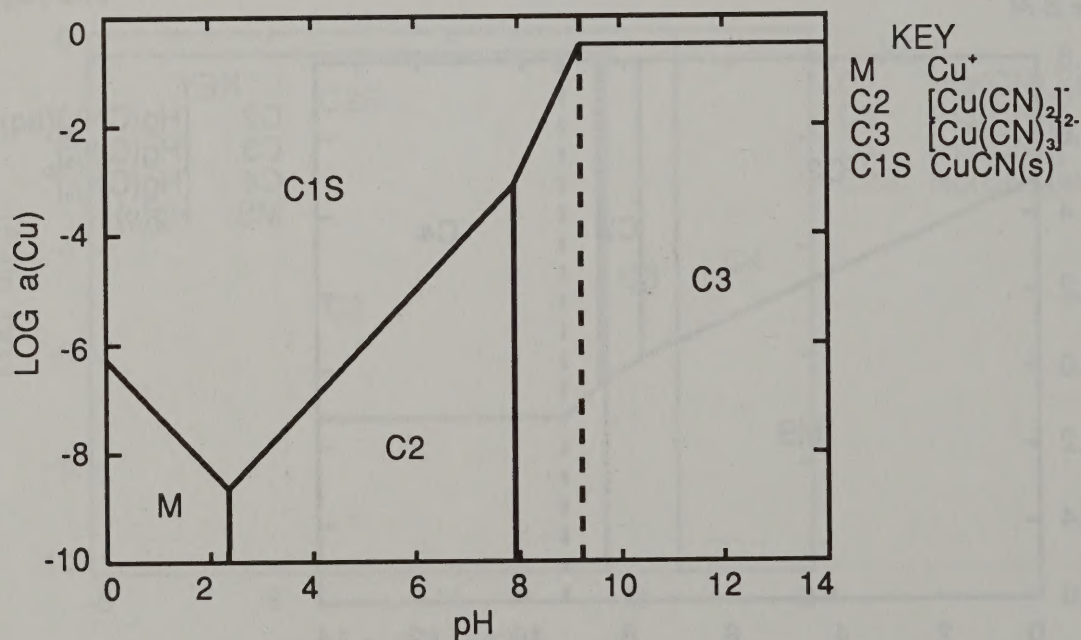


Figure E-75



$p\text{Cu(I)}$ - $p\text{H}$  diagram for  $p\text{CN} = 5.0$ .

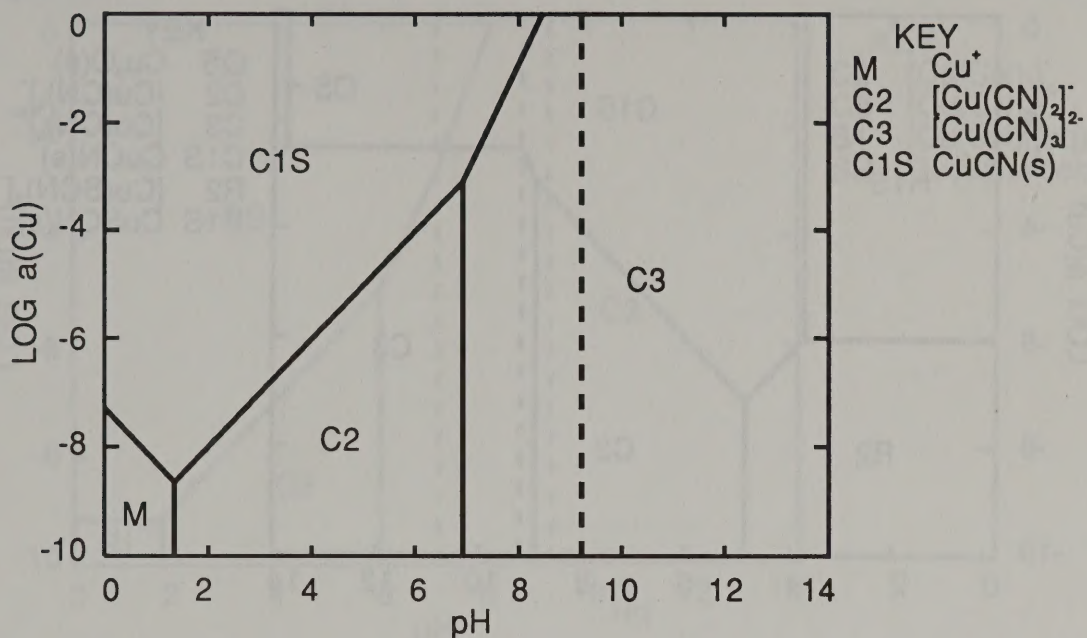
Figure E-76



$p\text{Cu(I)}$ - $p\text{H}$  diagram for  $p\text{CN} = 4.0$ .

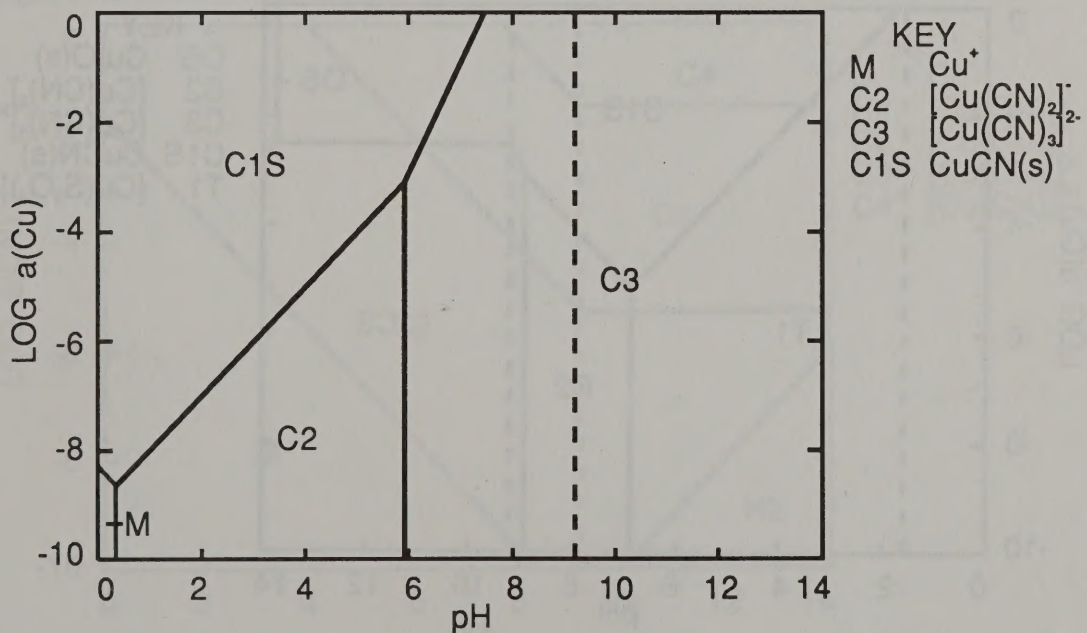


Figure E-77



$p\text{Cu(I)}\text{-pH}$  diagram for  $p\text{CN} = 3.0$ .

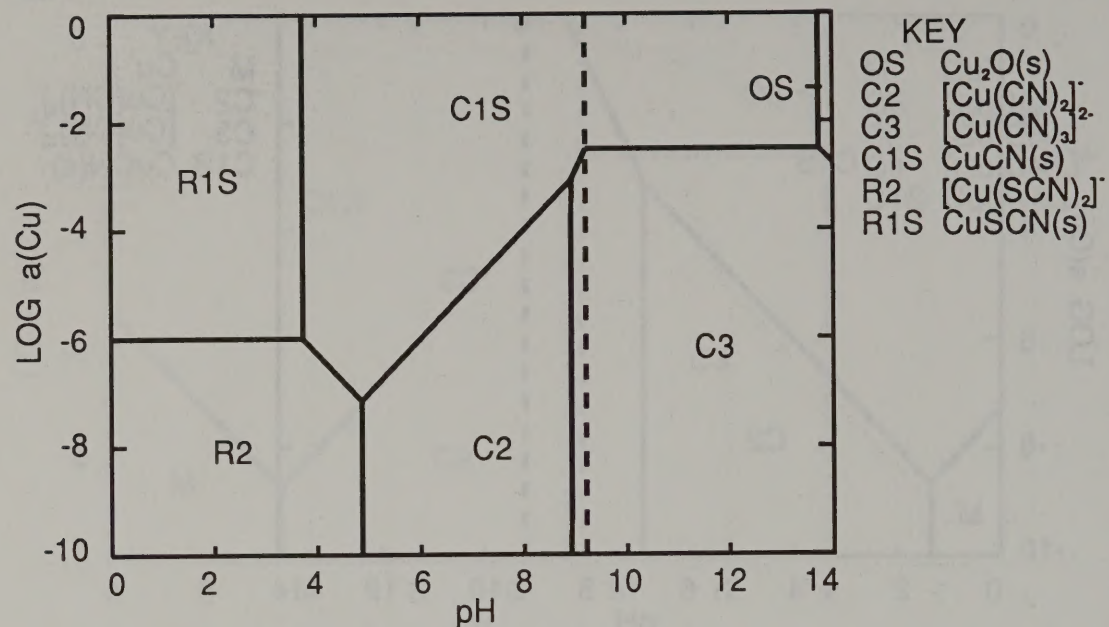
Figure E-78



$p\text{Cu(I)}\text{-pH}$  diagram for  $p\text{CN} = 2.0$ .

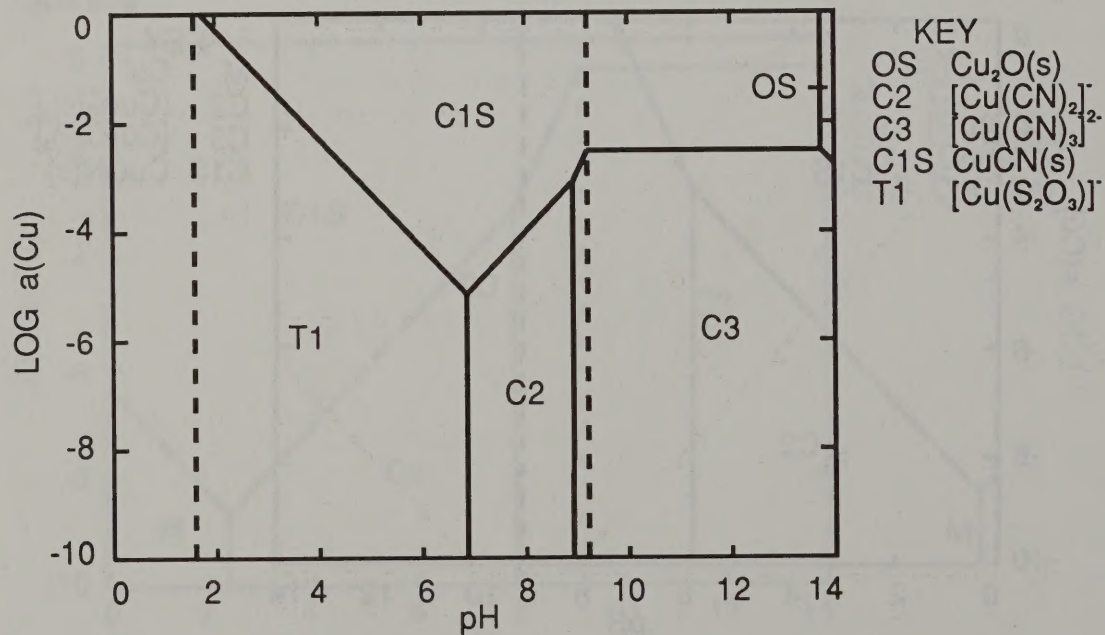


Figure E-79



*pCu(I)-pH diagram for  $p\text{CN} = 5.0$  and  $p\text{SCN} = 4.0$ .*

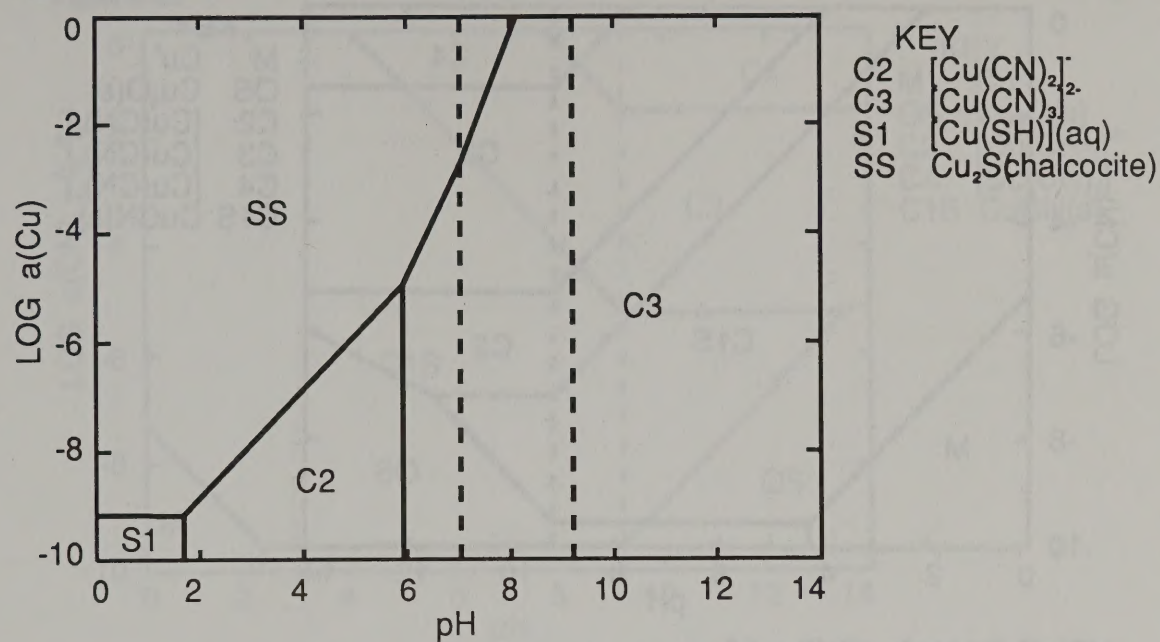
Figure E-80



*pCu(I)-pH diagram for  $p\text{CN} = 5.0$  and  $p\text{S}_2\text{O}_3 = 4.0$ .*

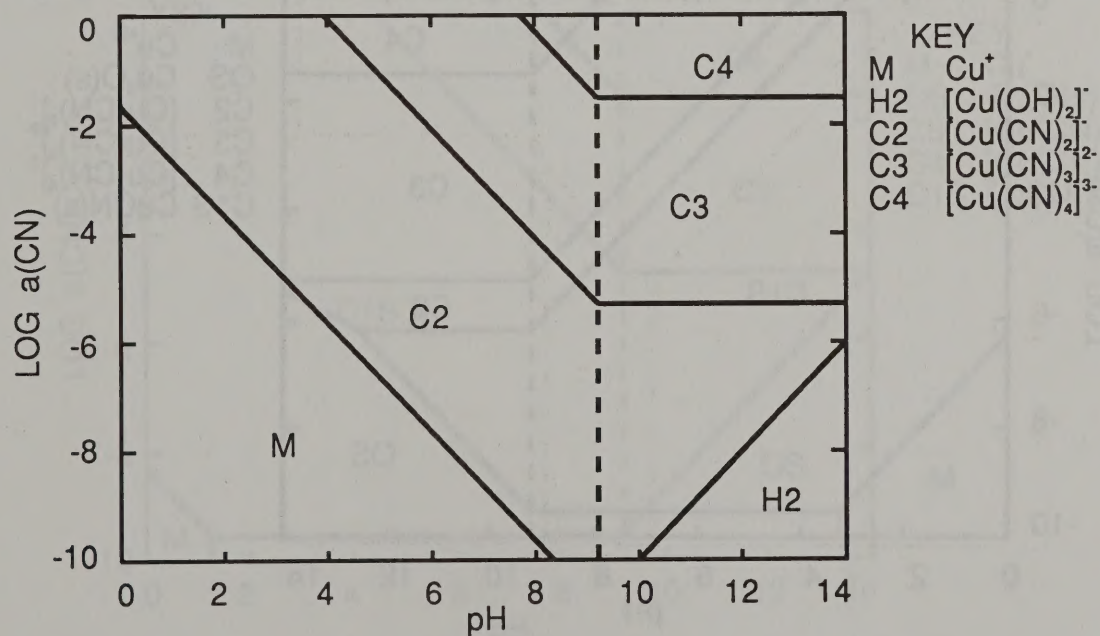


Figure E-81



$p\text{Cu(I)}$ - $\text{pH}$  diagram for  $p\text{CN} = 2.0$  and  $p\text{SH} = 6.0$ .

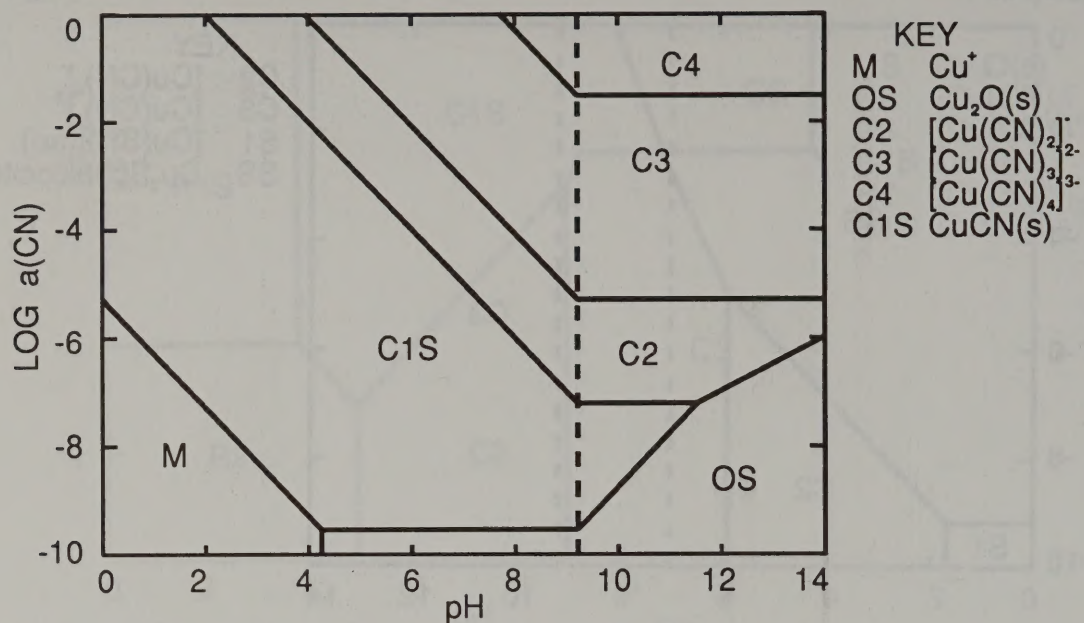
Figure E-82



$p\text{CN}$ - $\text{pH}$  diagram for copper(I) solution species.

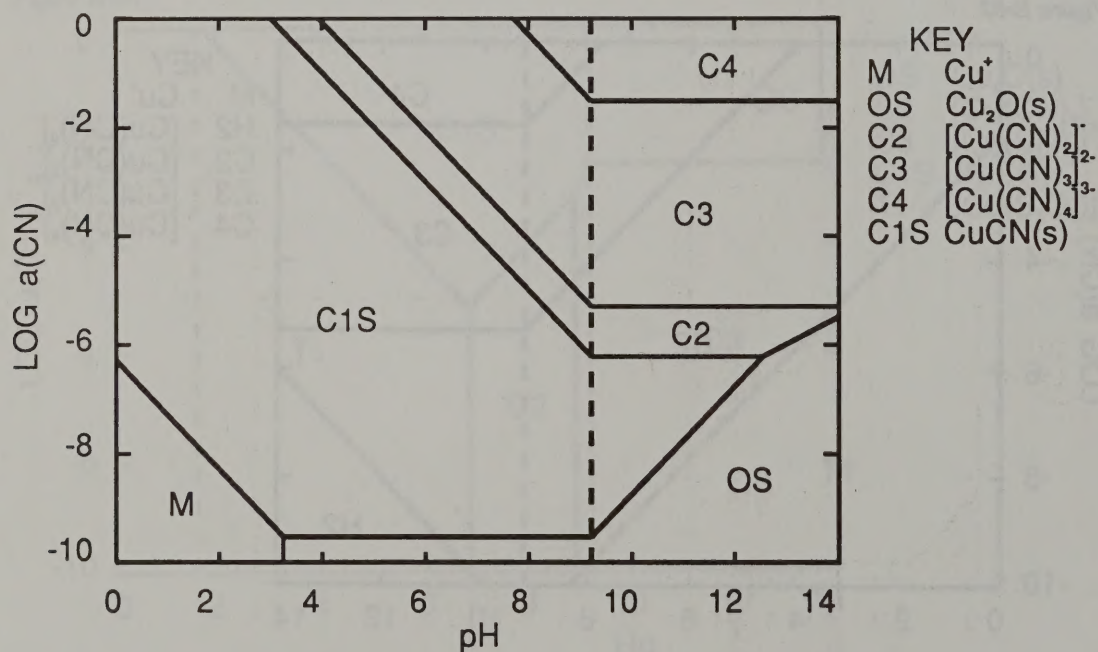


Figure E-83



*pCN-pH diagram for  $p\text{Cu(I)} = 5.0$ .*

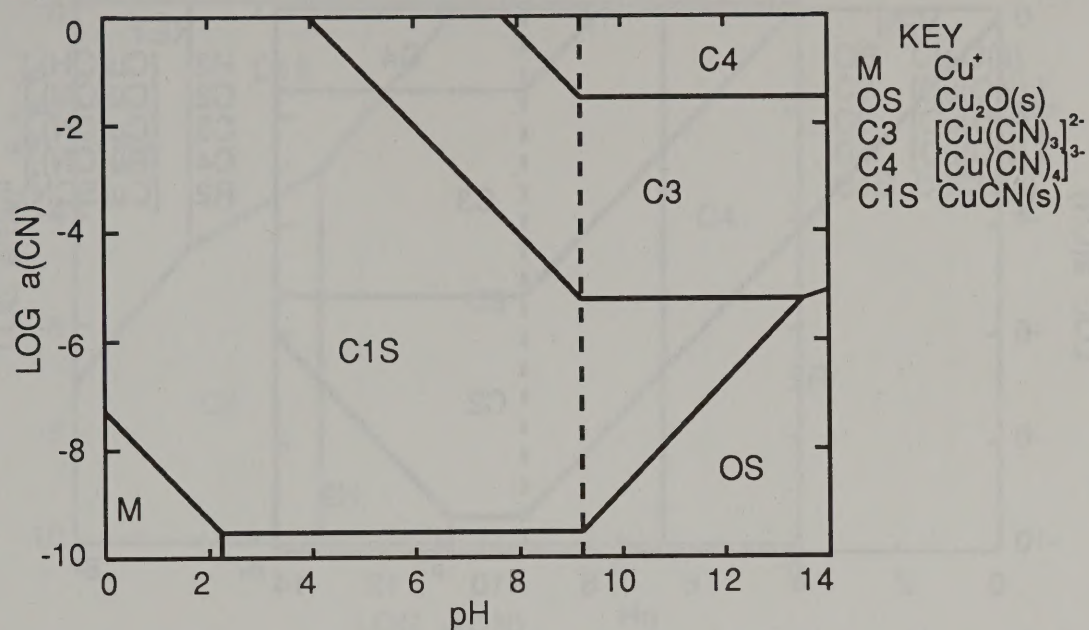
Figure E-84



*pCN-pH diagram for  $p\text{Cu(I)} = 4.0$ .*

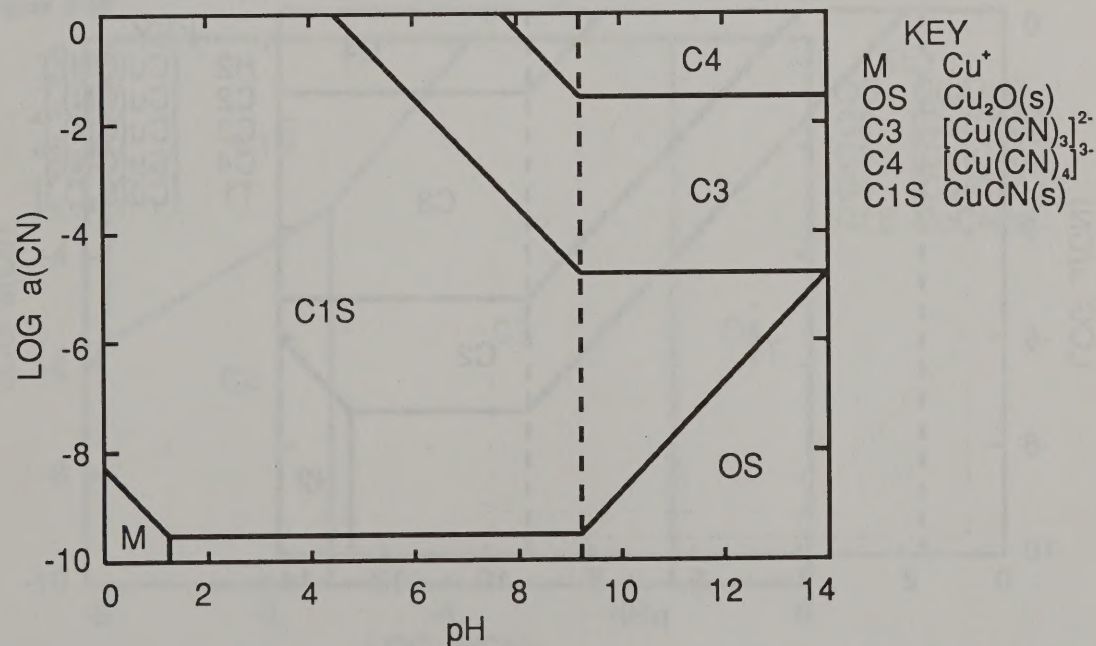


Figure E-85



*pCN-pH diagram for  $p\text{Cu(I)} = 3.0$ .*

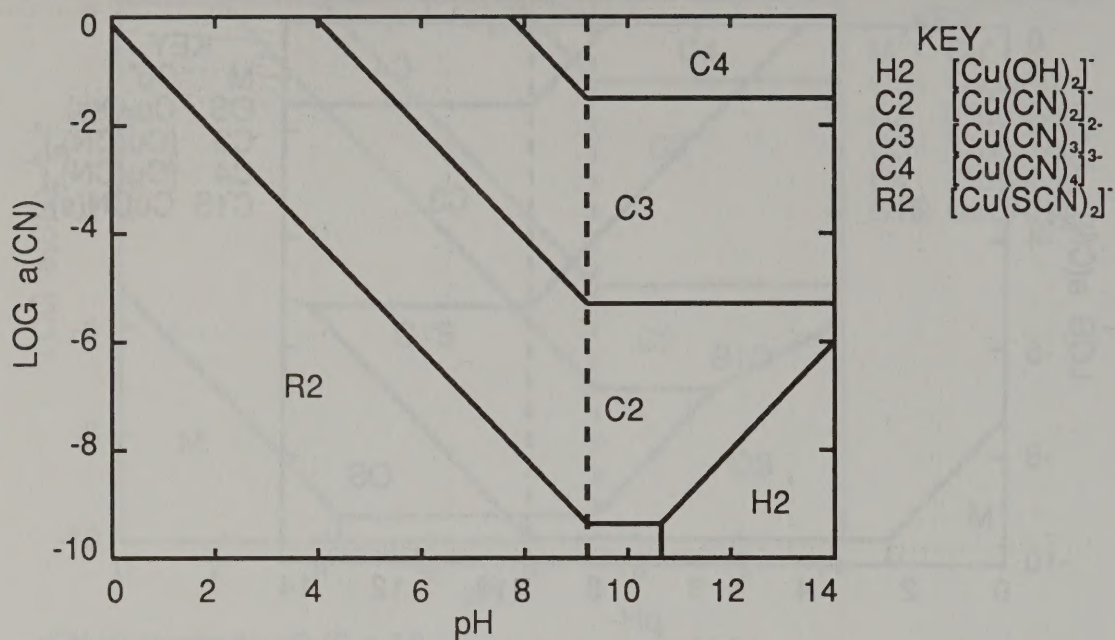
Figure E-86



*pCN-pH diagram for  $p\text{Cu(I)} = 2.0$ .*

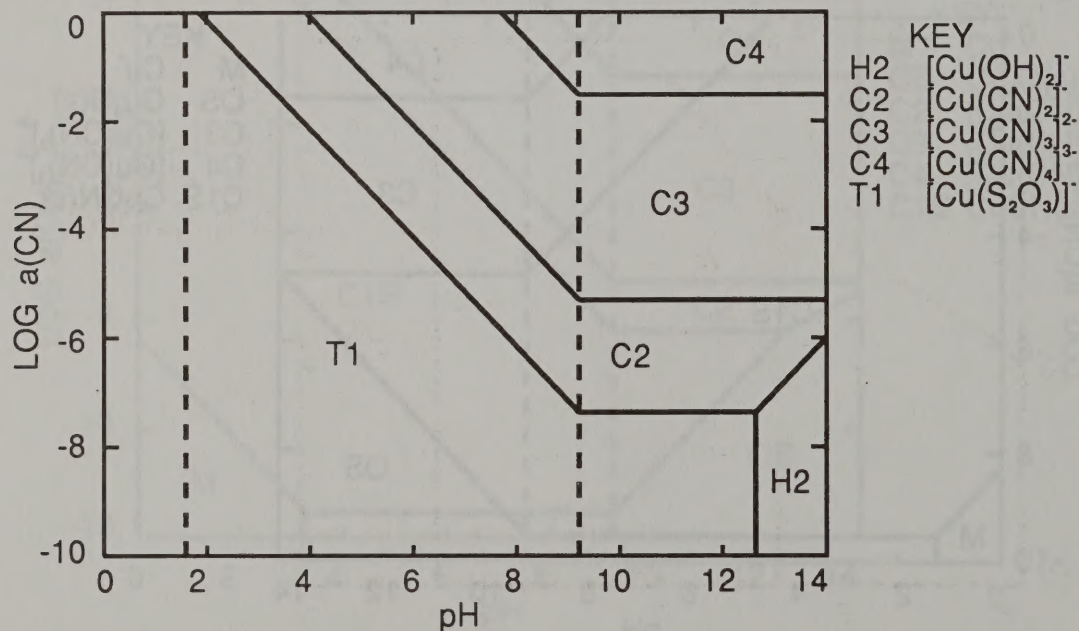


Figure E-87



*pCN-pH diagram for copper(I) solution species with  $pSCN = 4.0$ .*

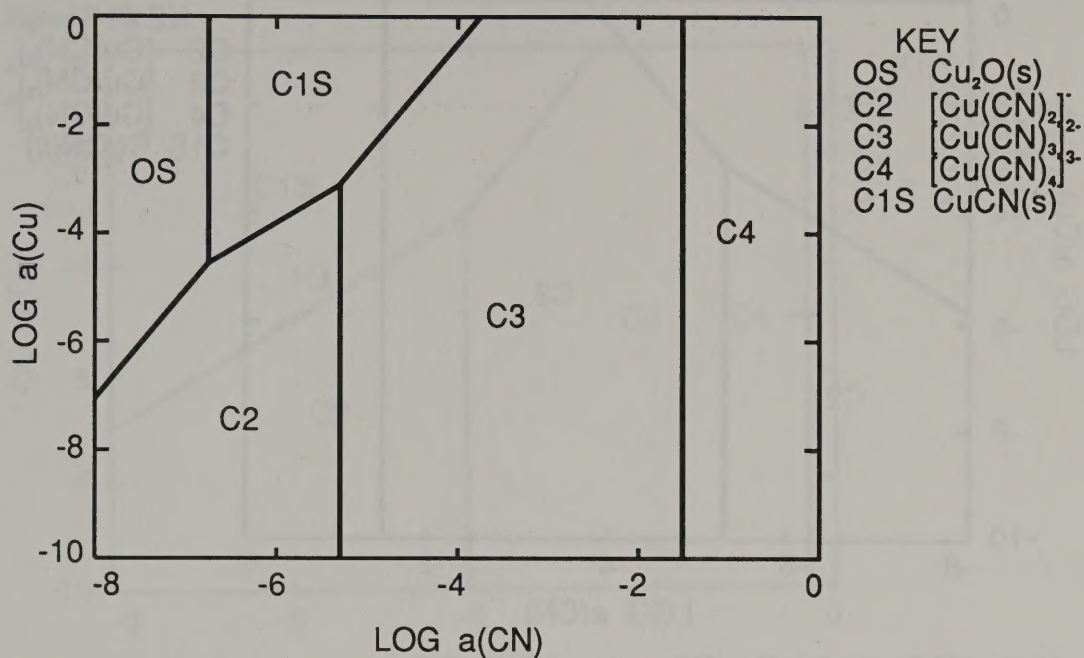
Figure E-88



*pCN-pH diagram for copper(I) solution species with  $pS_2O_3 = 4.0$ .*

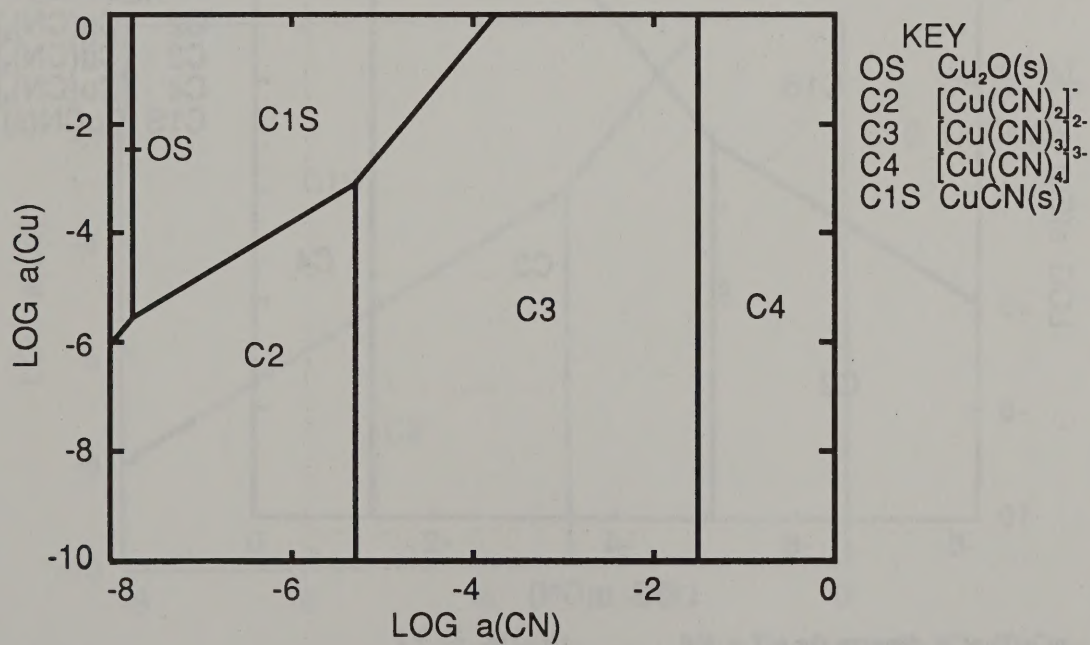


Figure E-89



*pCu(I)-pCN diagram for pH = 12.0.*

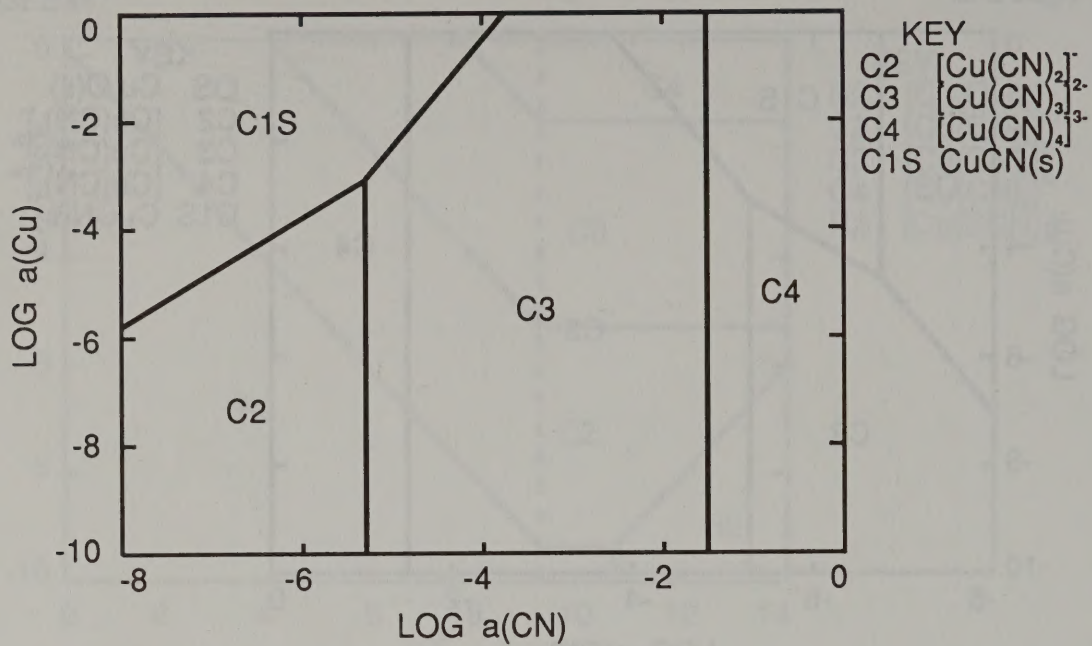
Figure E-90



*pCu(I)-pCN diagram for pH = 11.0.*

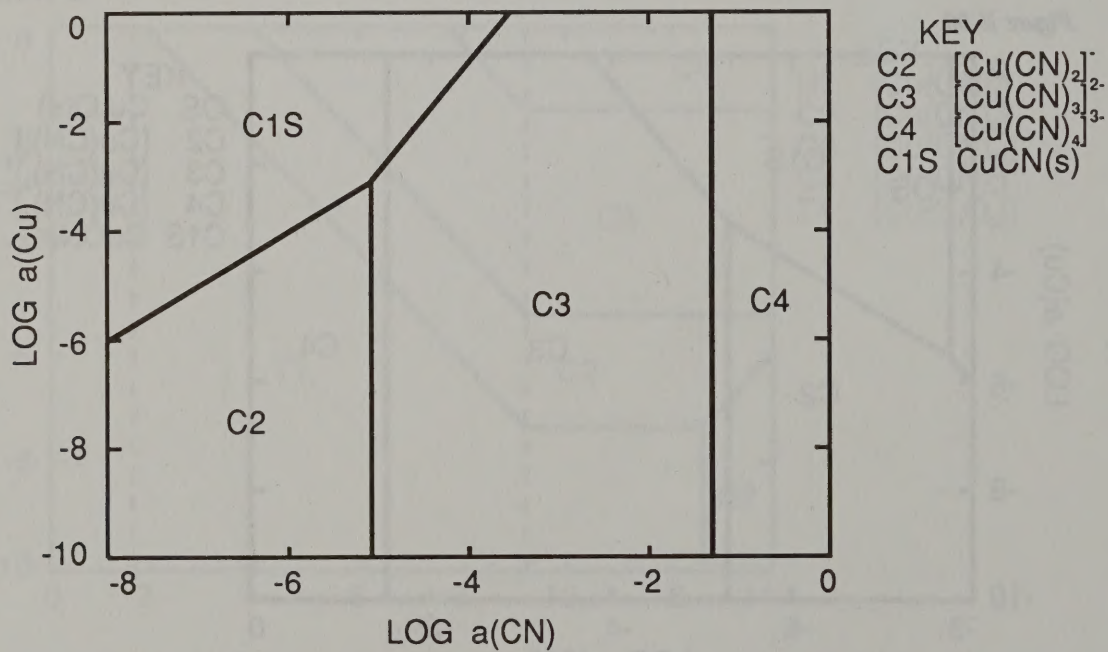


Figure E-91



*pCu(I)-pCN diagram for pH = 10.0.*

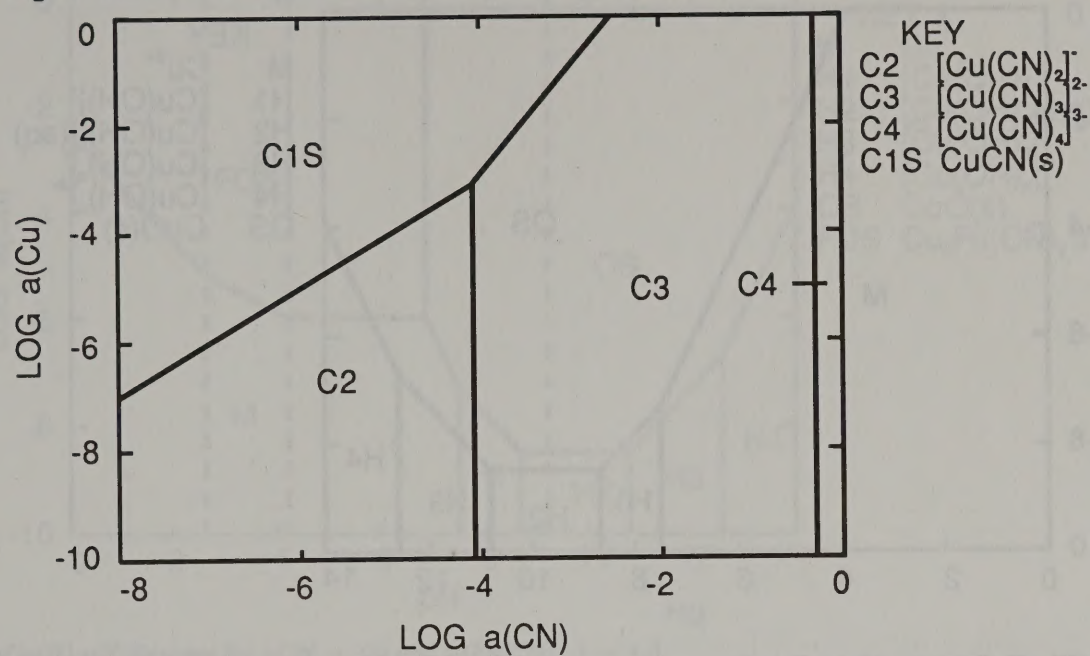
Figure E-92



*pCu(I)-pCN diagram for pH = 9.0.*

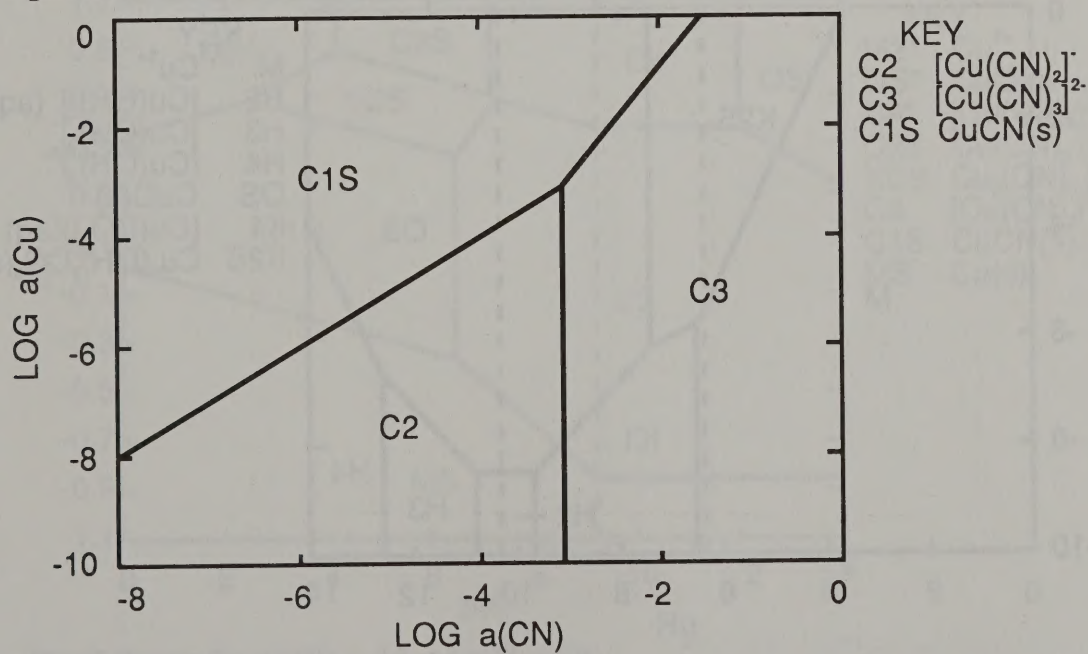


Figure E-93



*pCu(I)-pCN diagram for pH = 8.0.*

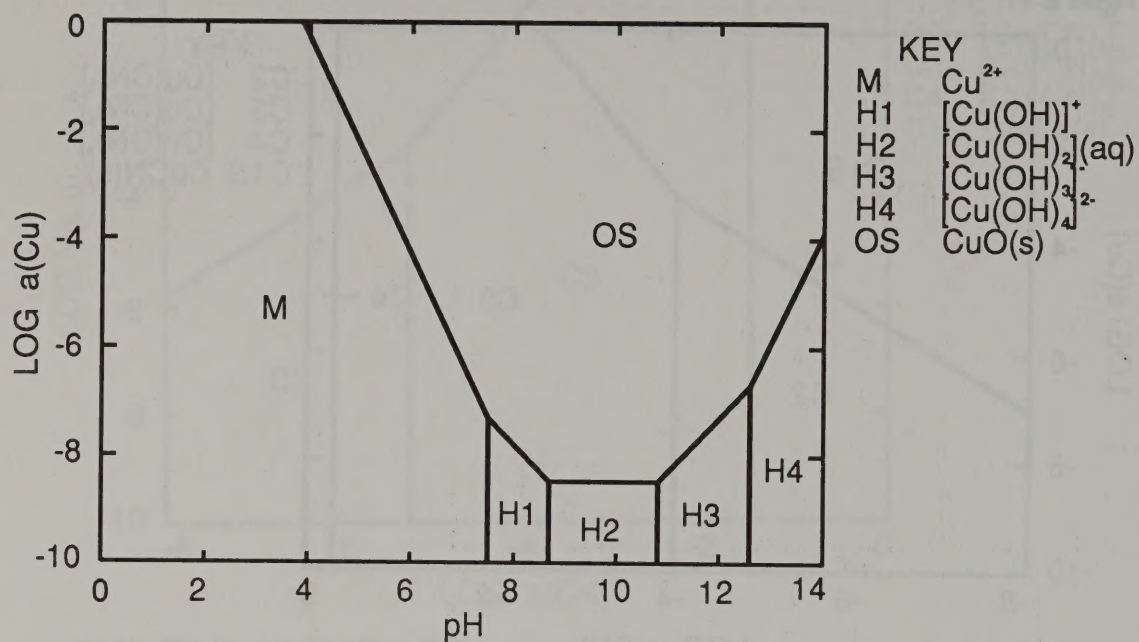
Figure E-94



*pCu(I)-pCN diagram for pH = 7.0.*

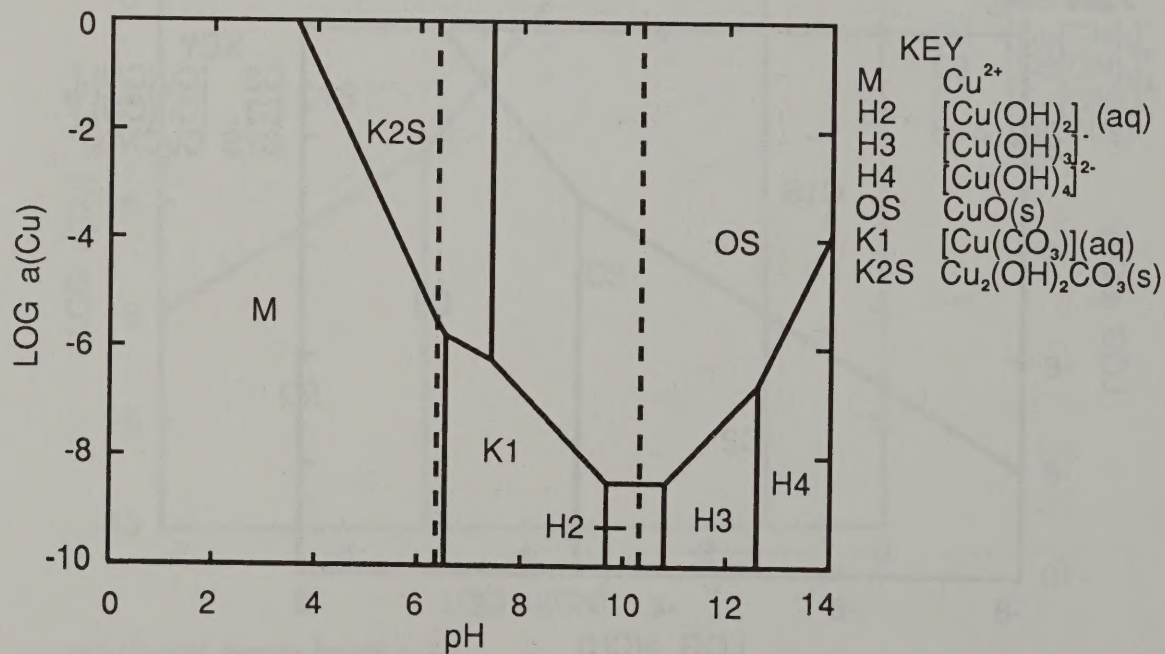


Figure E-95



$p\text{Cu(II)}$ -pH diagram with no ligands.

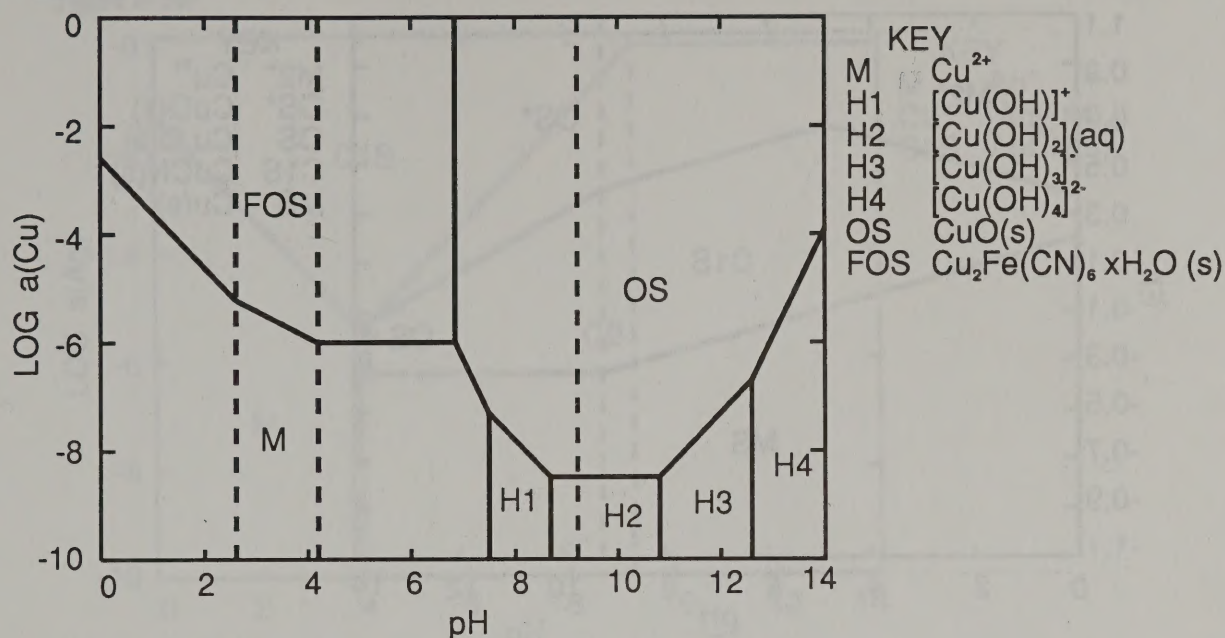
Figure E-96



$p\text{Cu(II)}$ -pH diagram for  $p\text{CO}_3 = 3.0$ .

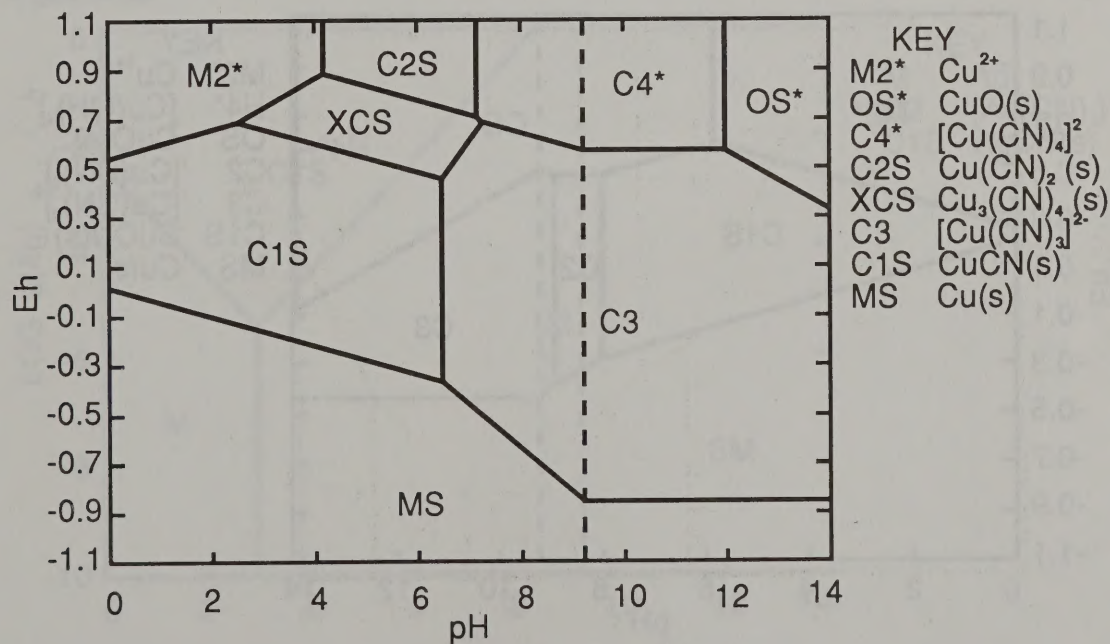


Figure E-97



$p\text{Cu}(\text{II})$ -pH diagram for  $p\text{CN} = 5.0$  and  $p[\text{Fe}(\text{CN})_6^{4-}] = 4.0$ .

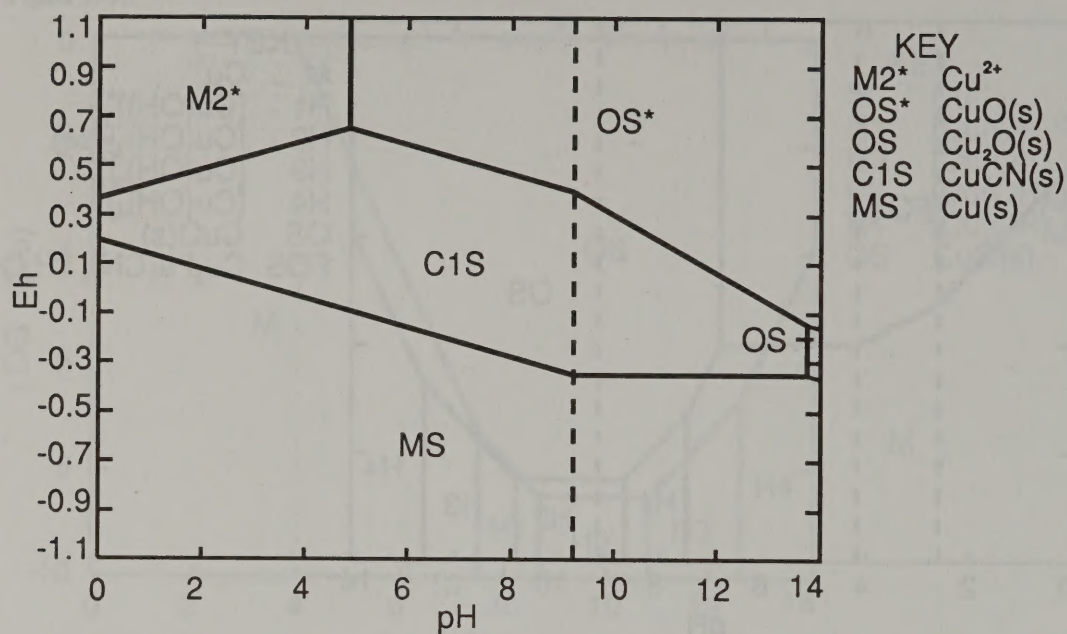
Figure E-98



$\text{Eh}$ -pH diagram for  $p\text{Cu}(\text{II}) = 2.0$  and  $p\text{CN} = 2.0$ .

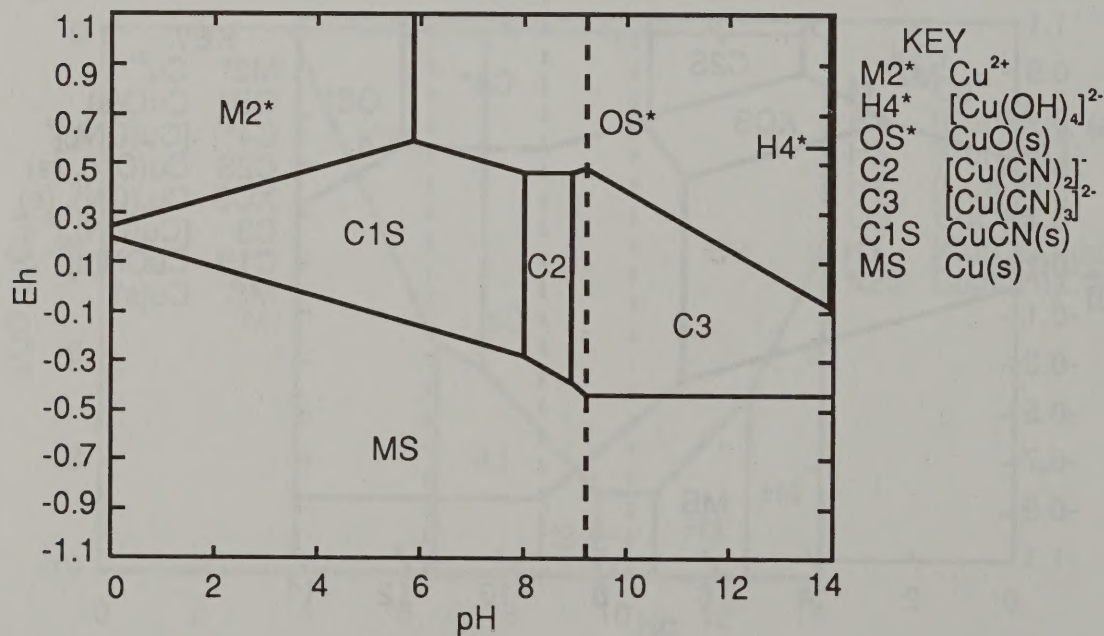


Figure E-99



*Eh-pH diagram for  $p\text{Cu(II)} = 2.0$  and  $p\text{CN} = 5.0$ .*

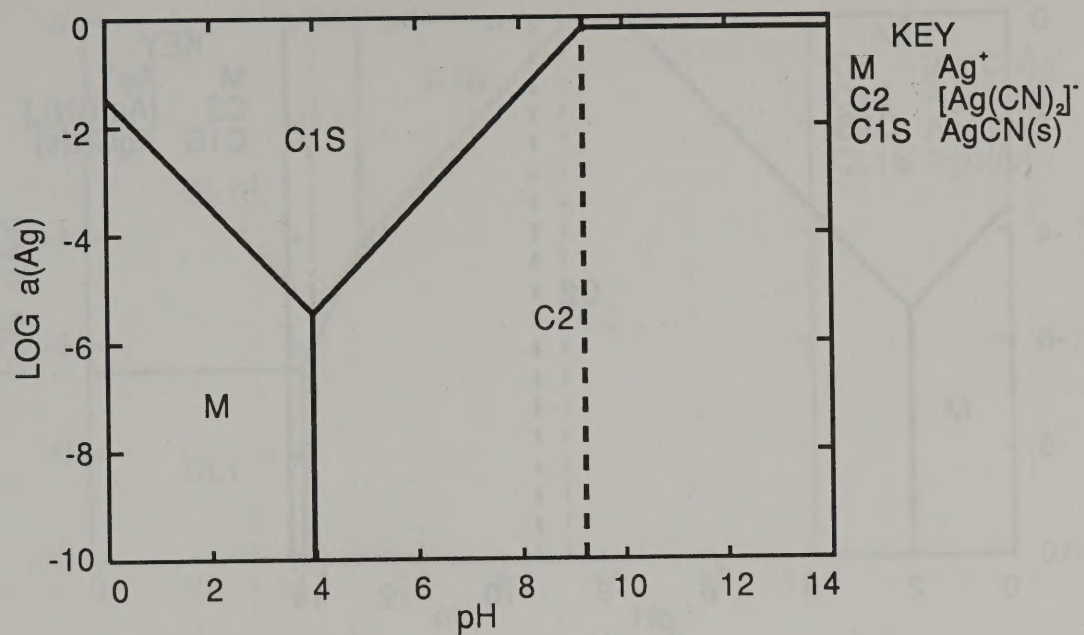
Figure E-100



*Eh-pH diagram for  $p\text{Cu(II)} = 4.0$  and  $p\text{CN} = 5.0$ .*

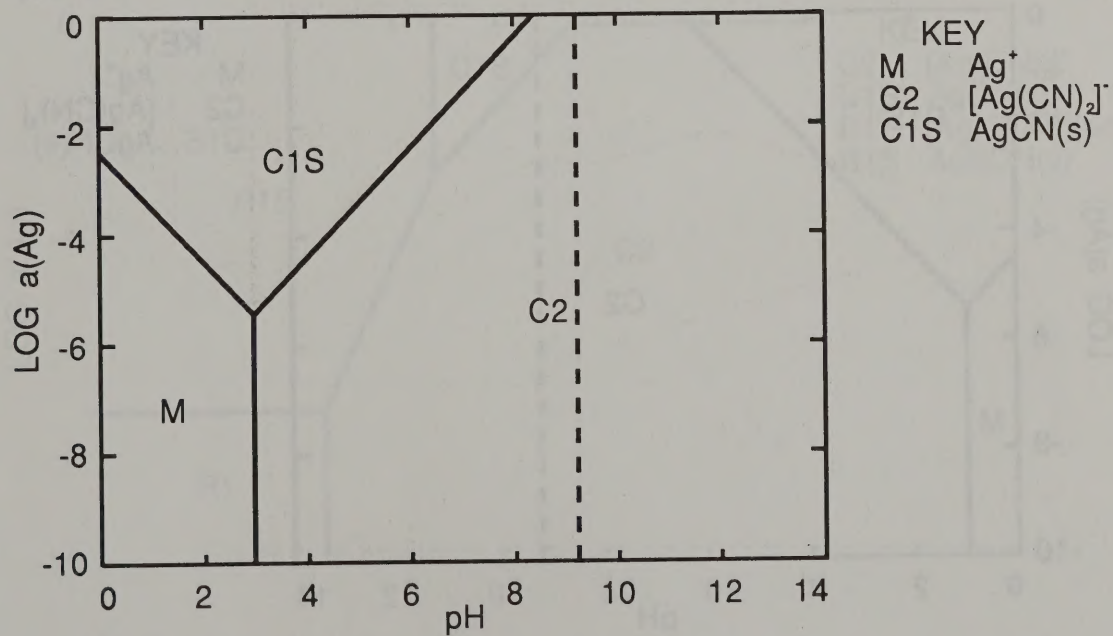


Figure E-101



$pAg$ - $pH$  diagram for  $pCN = 5.0$ .

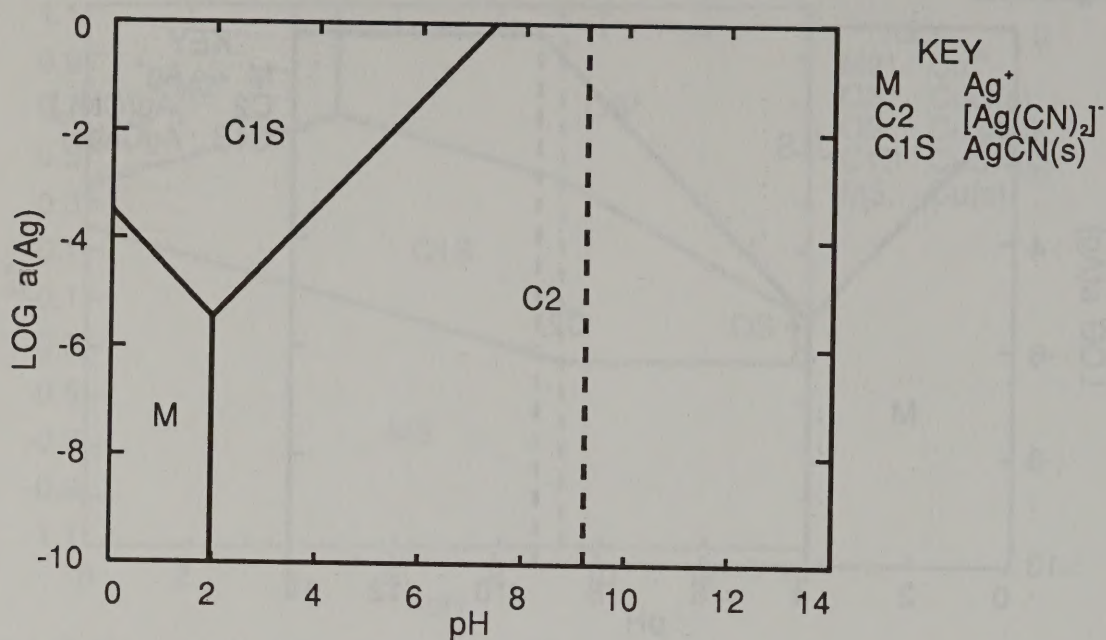
Figure E-102



$pAg$ - $pH$  diagram for  $pCN = 4.0$ .

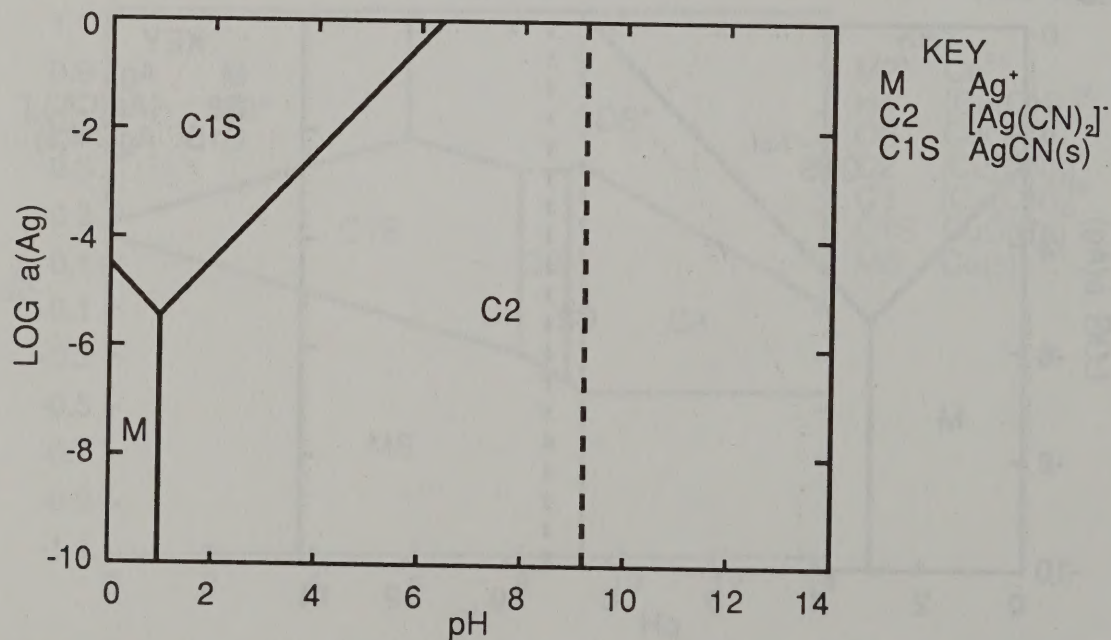


Figure E-103



*pAg-pH diagram for  $p\text{CN} = 3.0$ .*

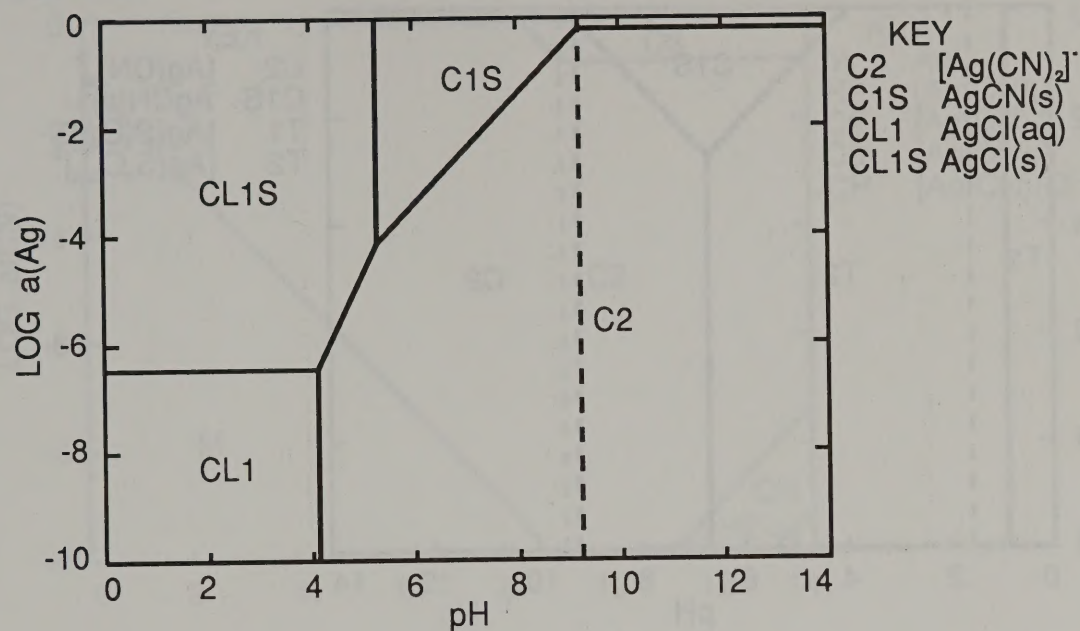
Figure E-104



*pAg-pH diagram for  $p\text{CN} = 2.0$ .*

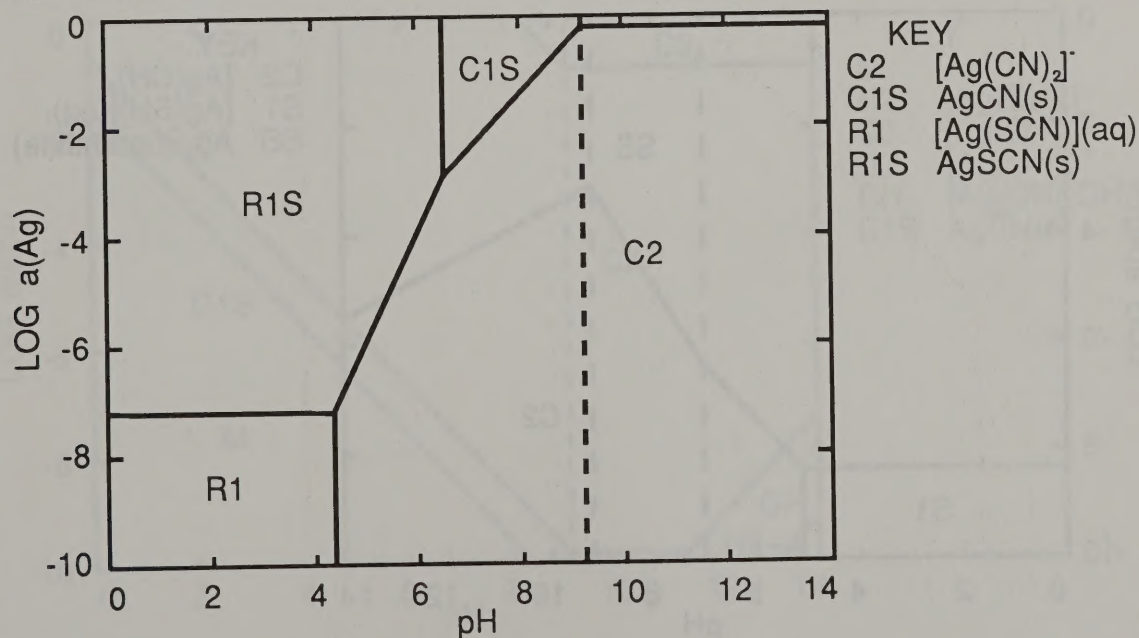


Figure E-105



*pAg-pH diagram for  $p\text{CN} = 5.0$  and  $p\text{Cl} = 3.0$ .*

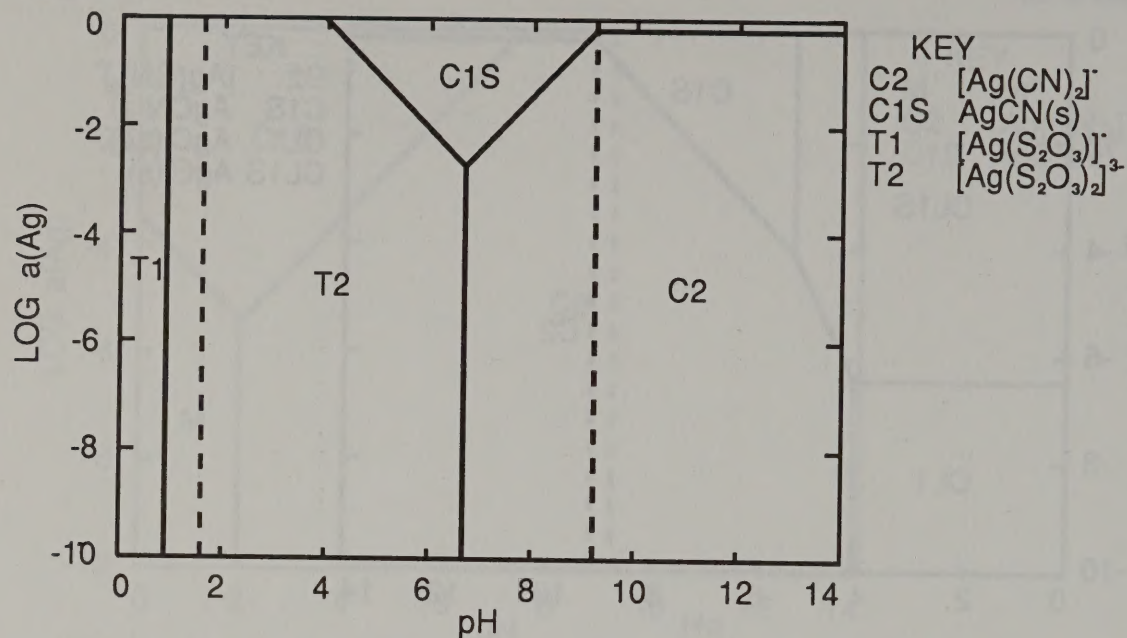
Figure E-106



*pAg-pH diagram for  $p\text{CN} = 5.0$  and  $p\text{SCN} = 4.0$ .*

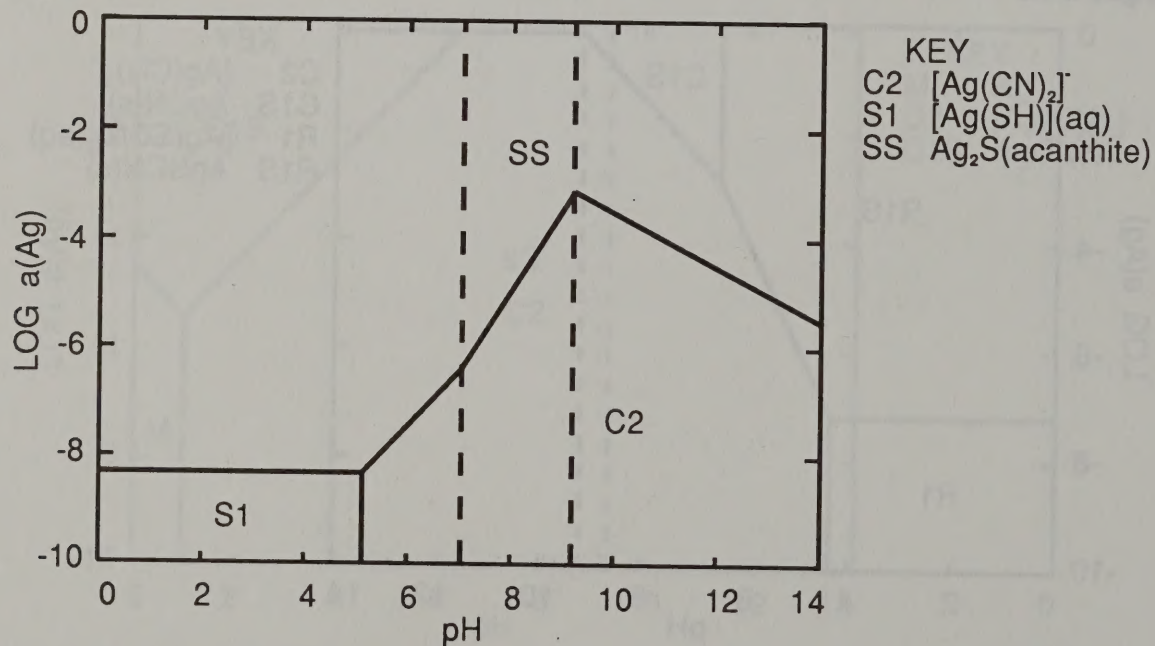


Figure E-107



*pAg-pH diagram for  $p\text{CN} = 5.0$  and  $p\text{S}_2\text{O}_3 = 4.0$ .*

Figure E-108



*pAg-pH diagram for  $p\text{CN} = 2.0$  and  $p\text{SH} = 6.0$ .*



Figure E-109

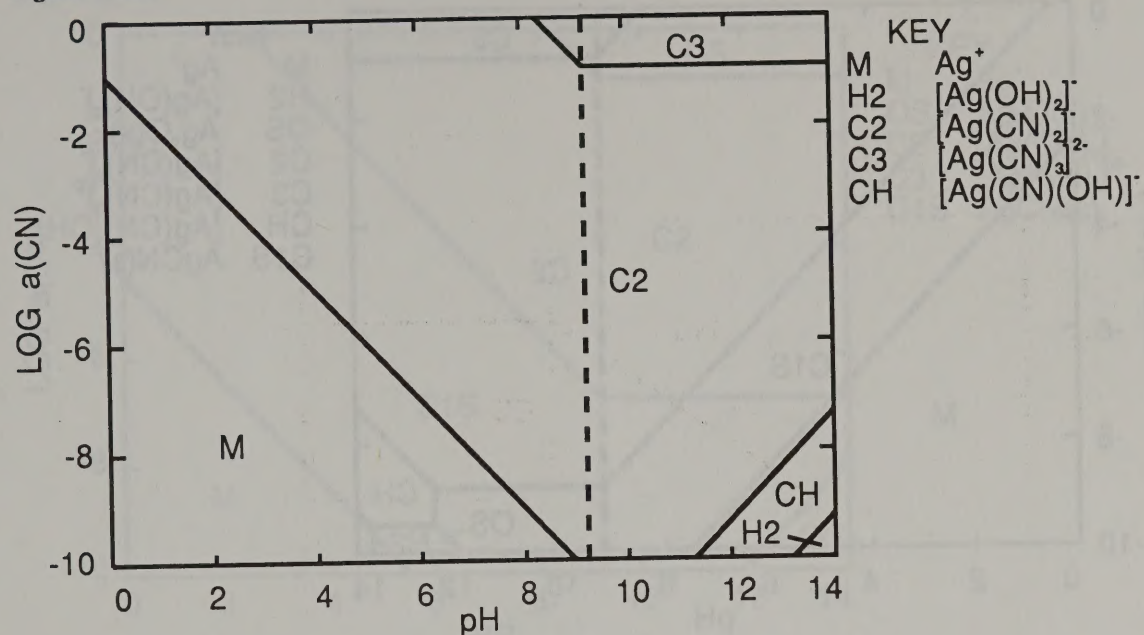
*pCN-pH diagram for silver solution species.*

Figure E-110

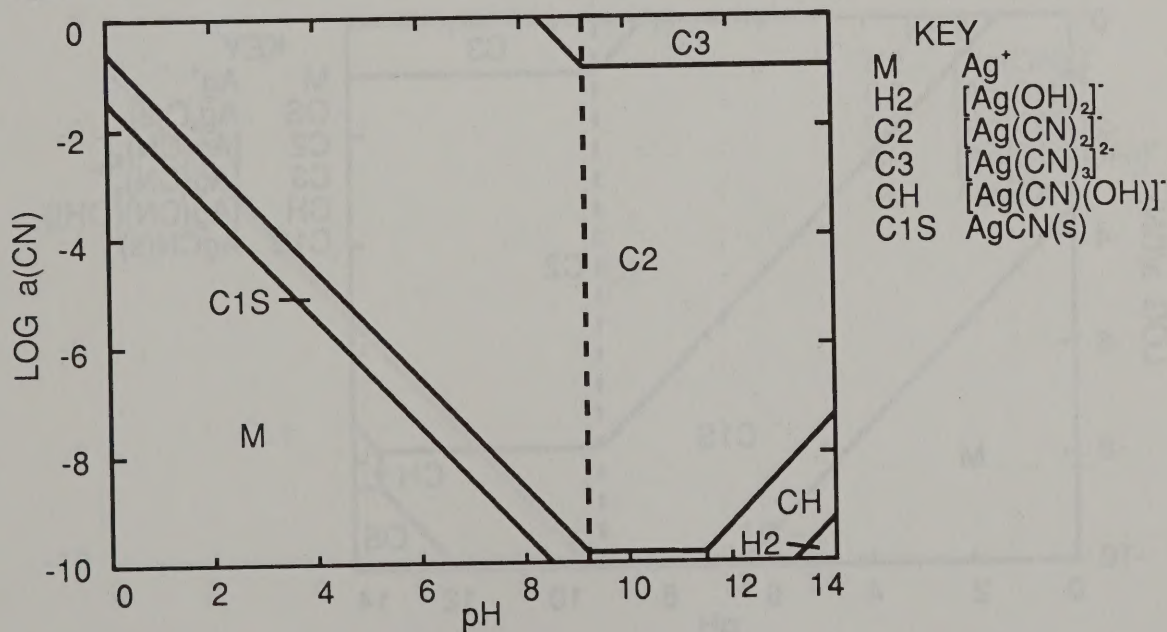
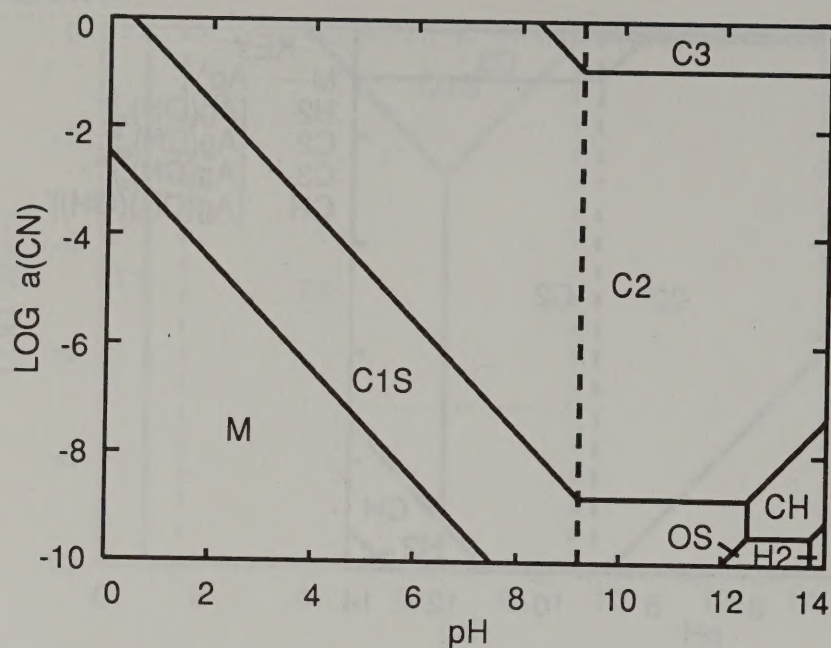
*pCN-pH diagram for  $p\text{Ag} = 5.0$ .*

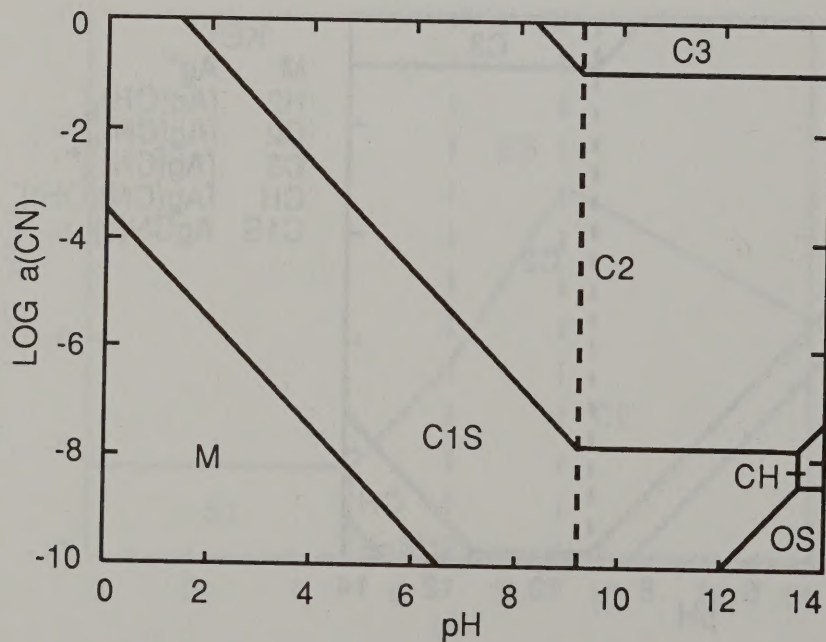


Figure E-111



*pCN-pH diagram for  $p\text{Ag} = 4.0$ .*

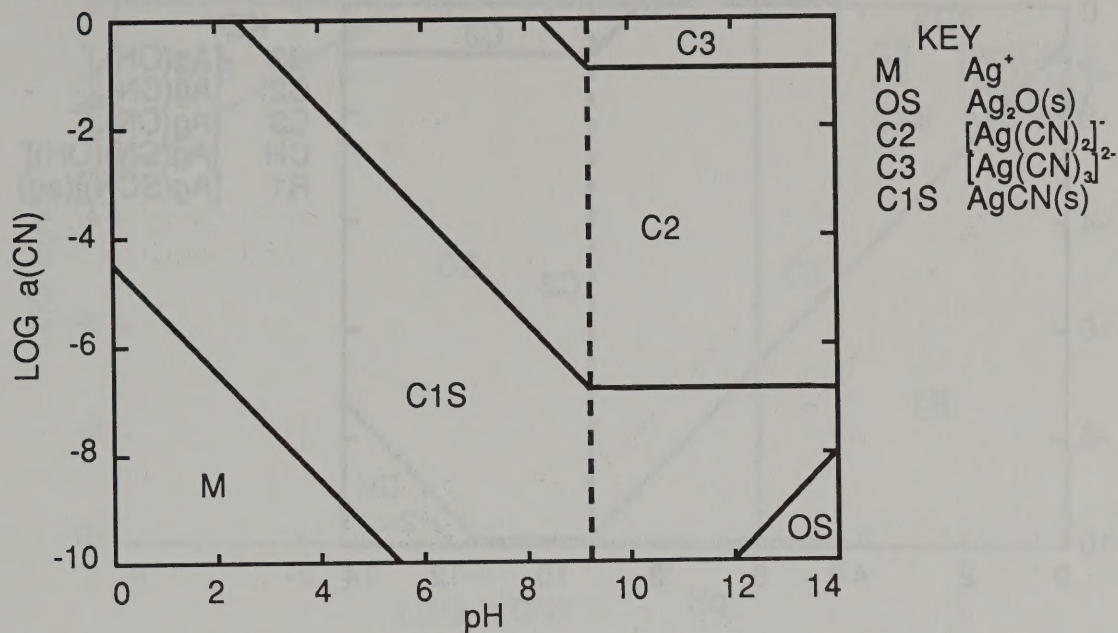
Figure E-112



*pCN-pH diagram for  $p\text{Ag} = 3.0$ .*

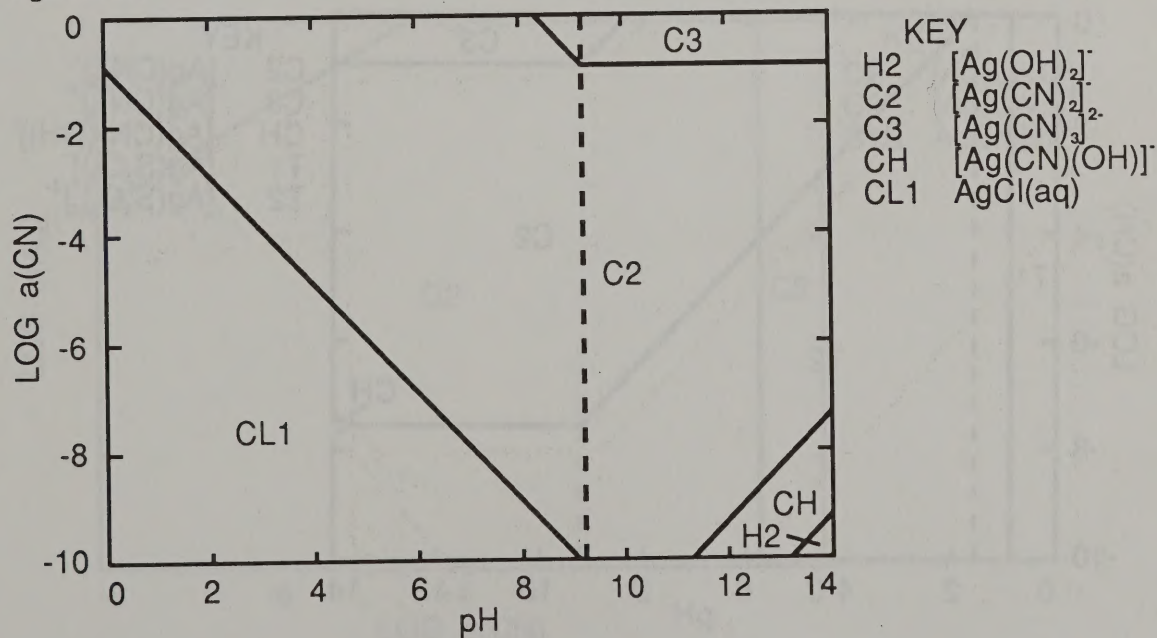


Figure E-113



*pCN-pH diagram for  $pAg = 2.0$ .*

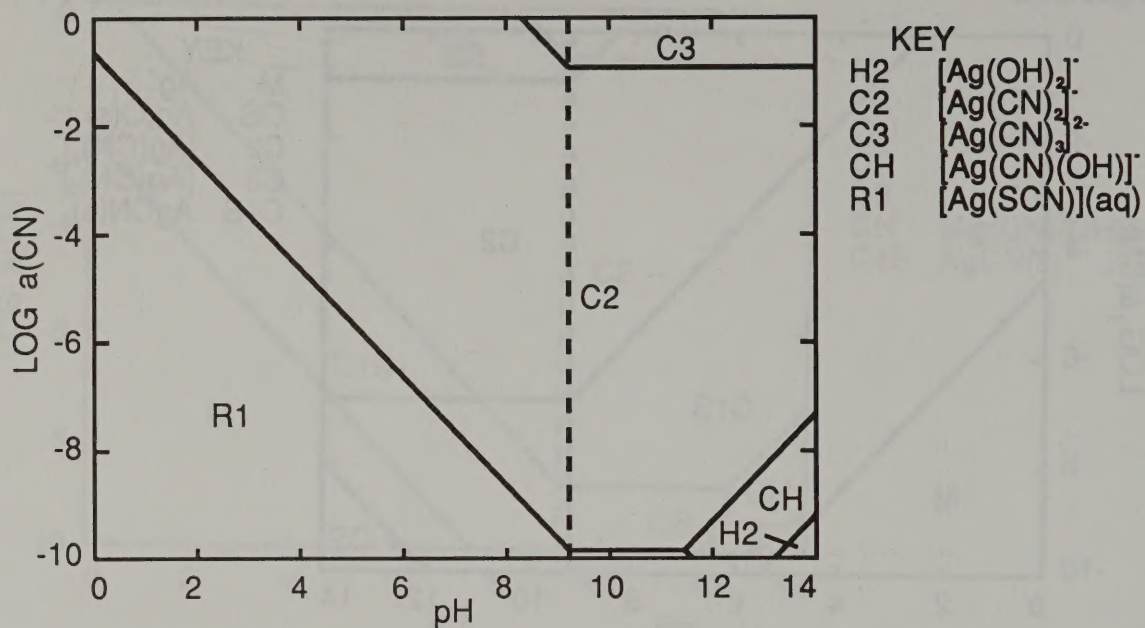
Figure E-114



*pCN-pH diagram for silver solution species with  $pCl = 3.0$ .*

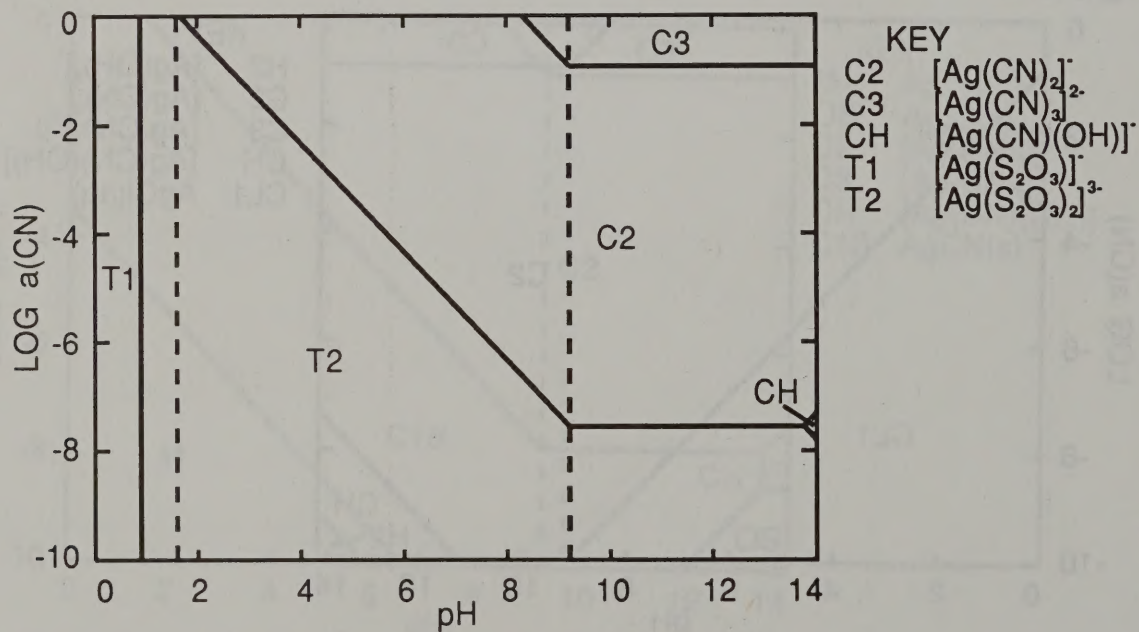


Figure E-115



pCN-pH diagram for silver solution species with  $pSCN = 4.0$ .

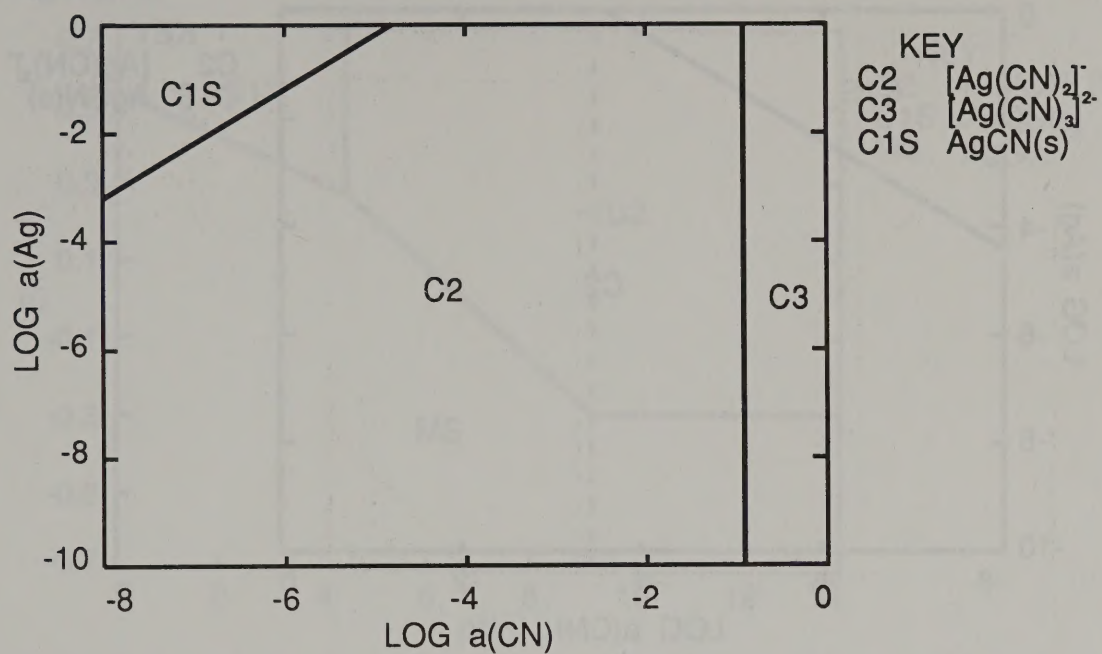
Figure E-116



pCN-pH diagram for silver solution species with  $pS_2O_3 = 4.0$ .

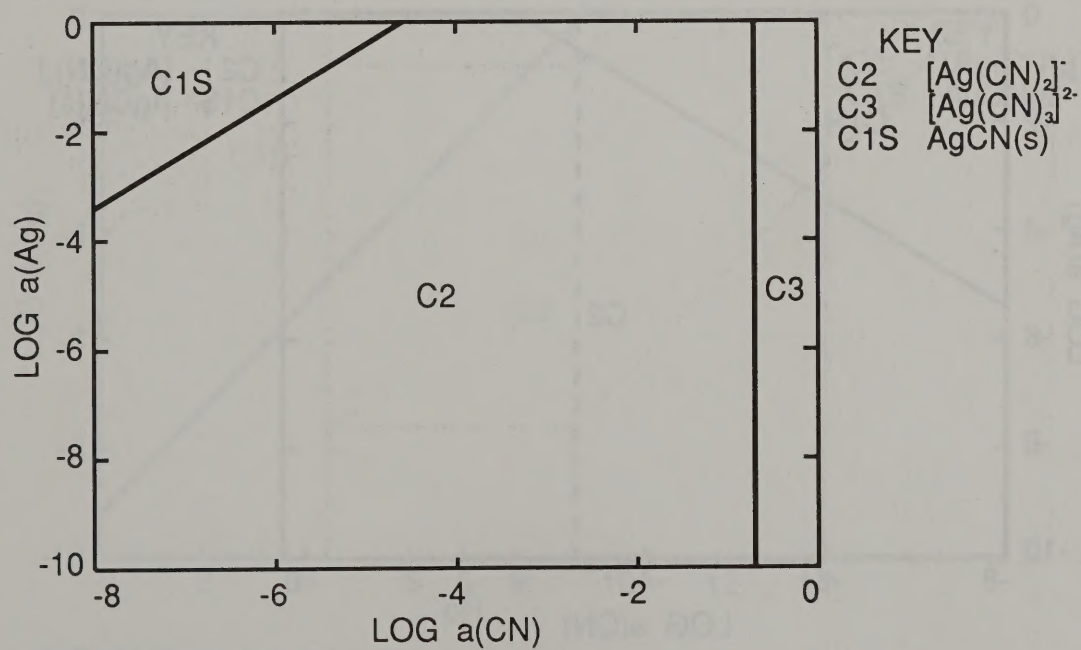


Figure E-117



$pAg$ - $pCN$  diagram for  $pH = 11.0$ .

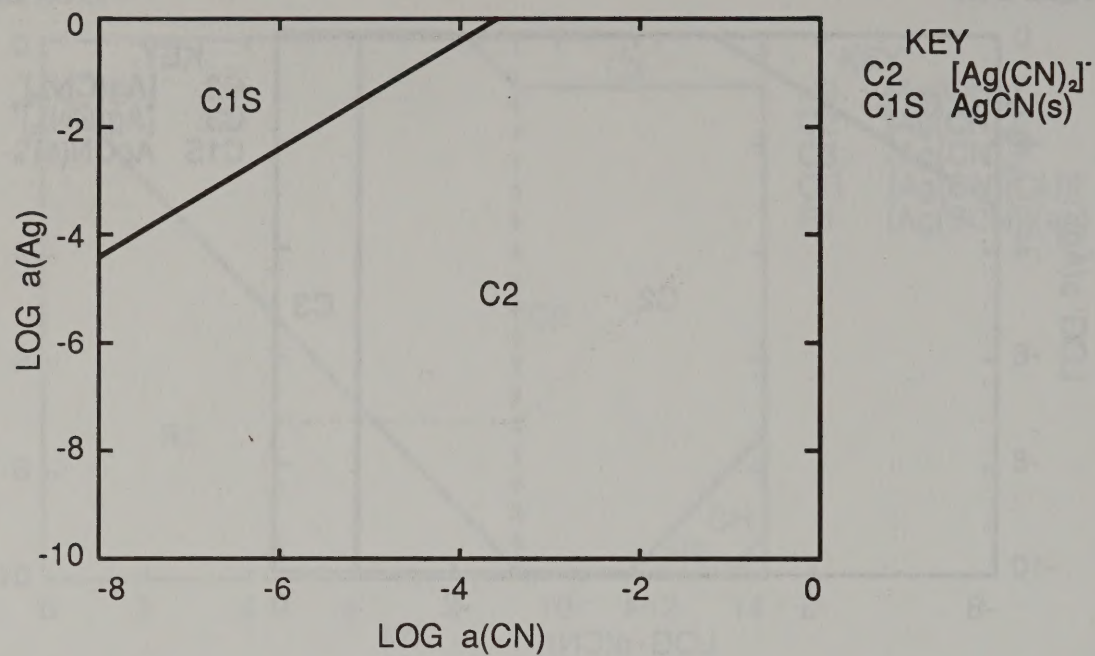
Figure E-118



$pAg$ - $pCN$  diagram for  $pH = 9.0$ .

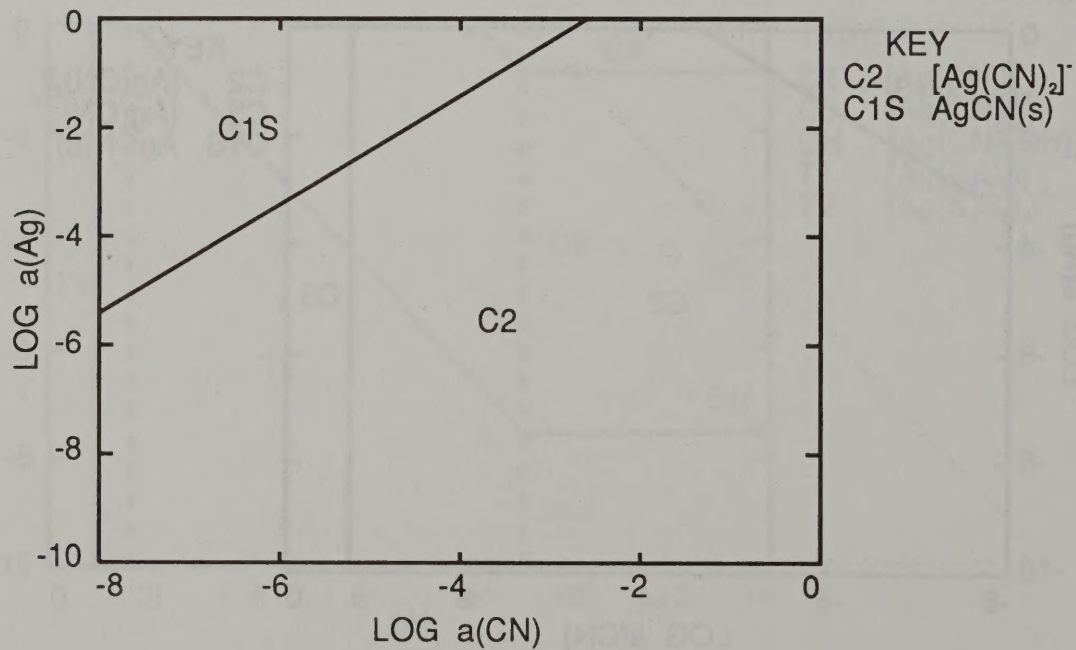


Figure E-119



*pAg-pCN diagram for pH = 8.0.*

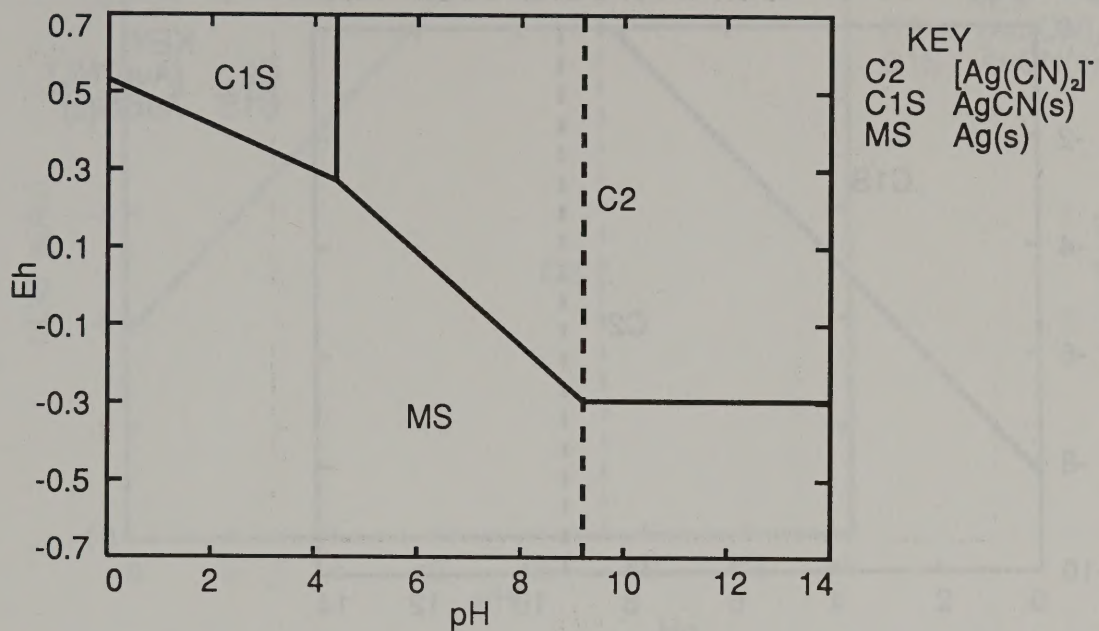
Figure E-120



*pAg-pCN diagram for pH = 7.0.*

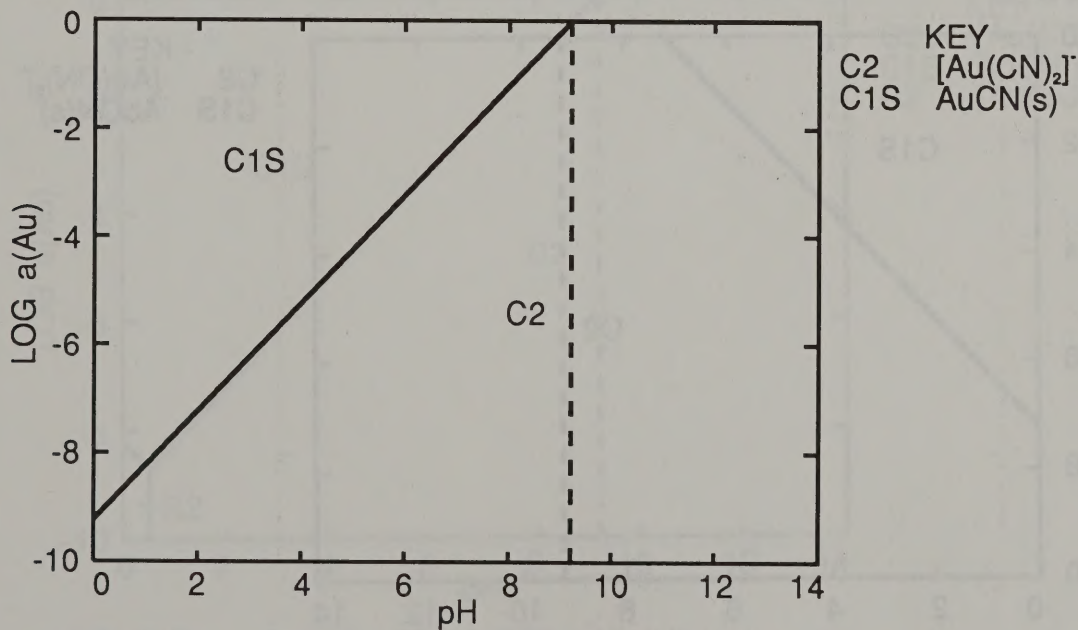


Figure E-121



*Eh-pH diagram for  $p\text{Ag} = 2.0$  and  $p\text{CN} = 2.0$ .*

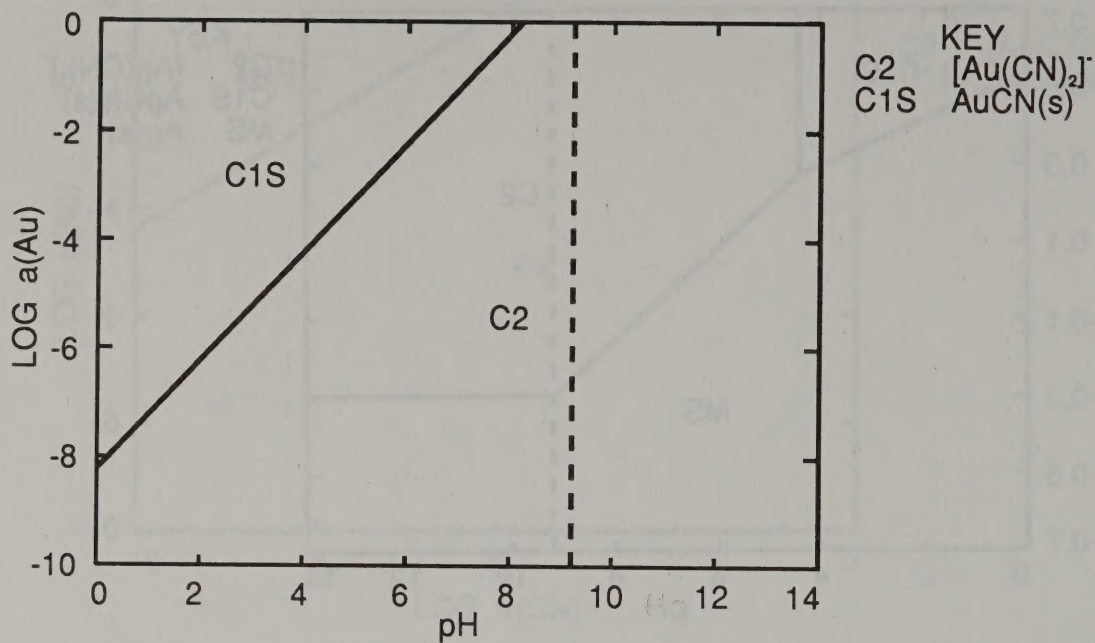
Figure E-122



*$p\text{Au(I)}$ -pH diagram for  $p\text{CN} = 5.0$ .*

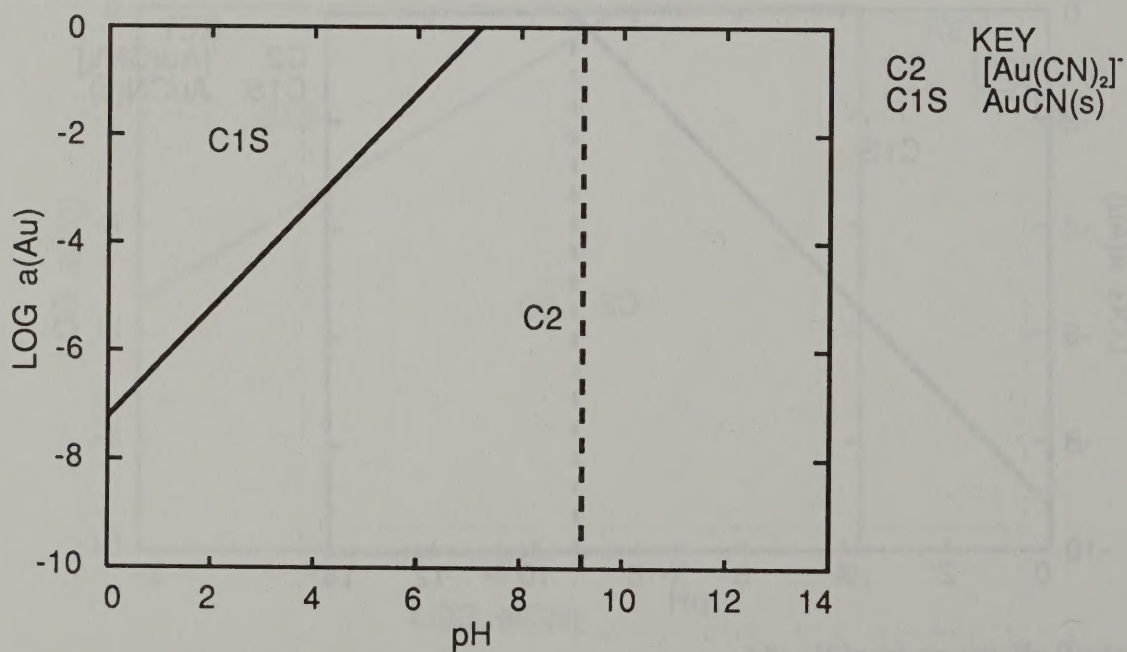


Figure E-123



$pAu(I)$ - $pH$  diagram for  $pCN = 4.0$ .

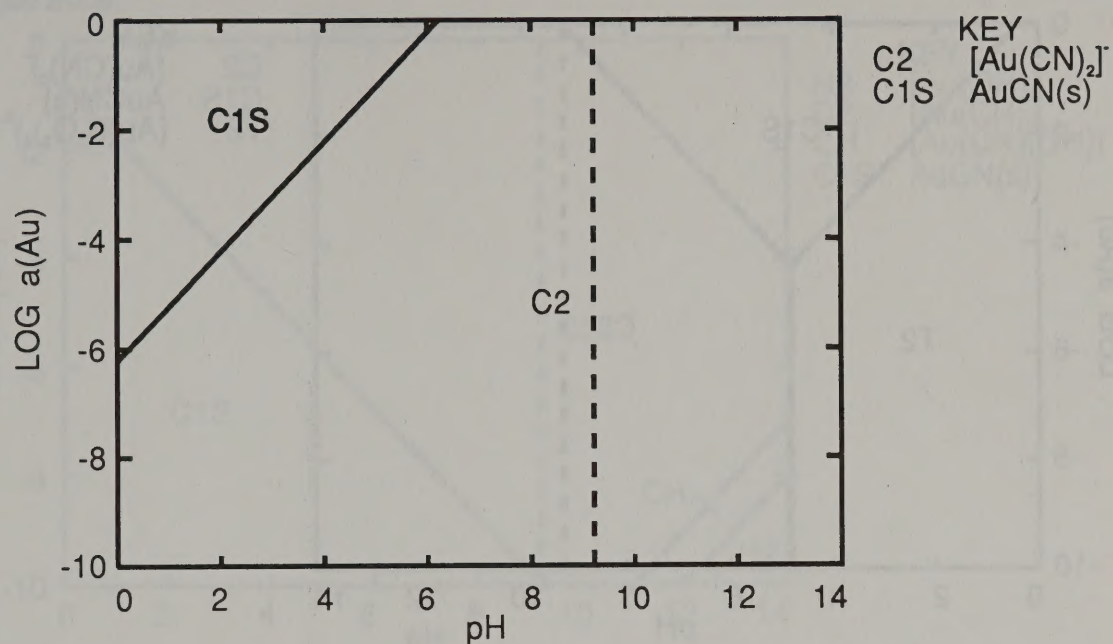
Figure E-124



$pAu(I)$ - $pH$  diagram for  $pCN = 3.0$ .

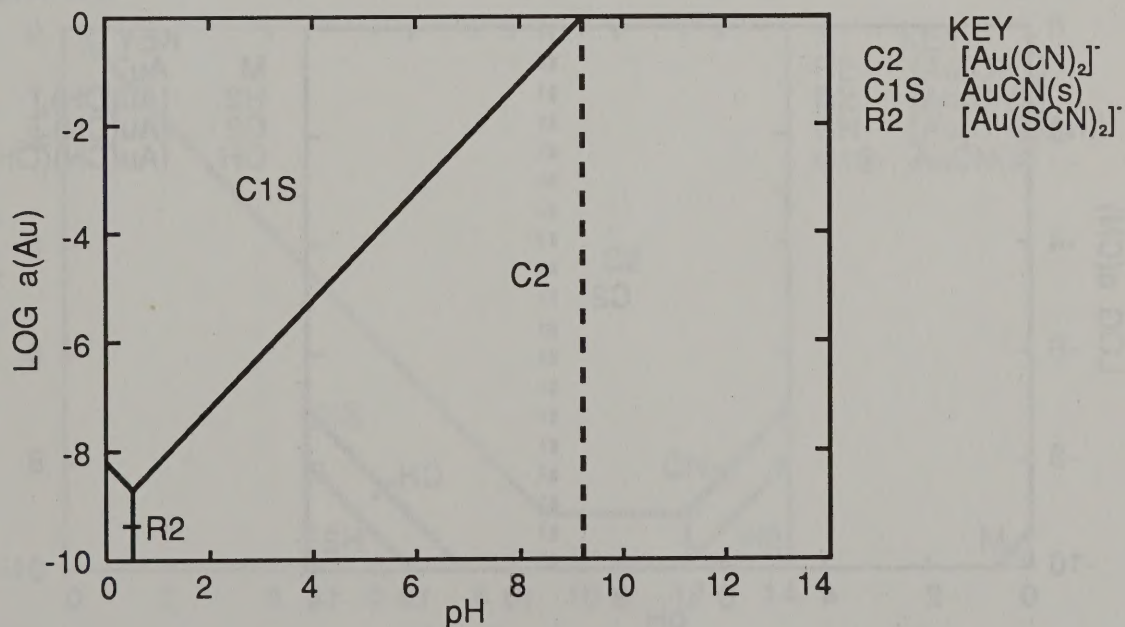


Figure E-125



$pAu(I)$ - $pH$  diagram for  $pCN = 2.0$ .

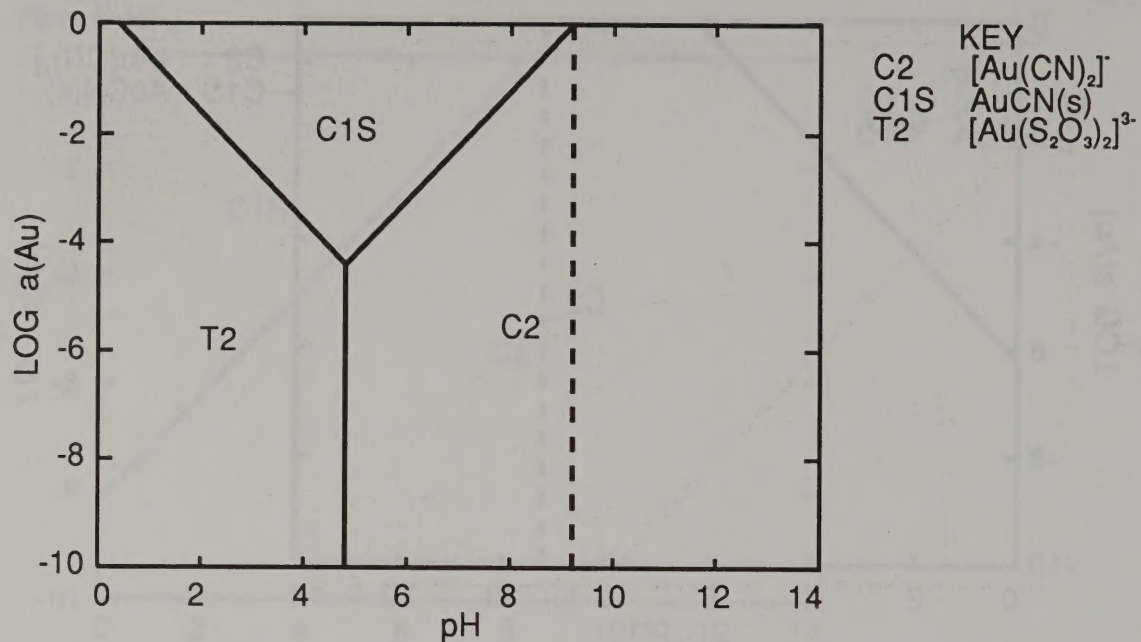
Figure E-126



$pAu(I)$ - $pH$  diagram for  $pCN = 5.0$  and  $pSCN = 4.0$ .

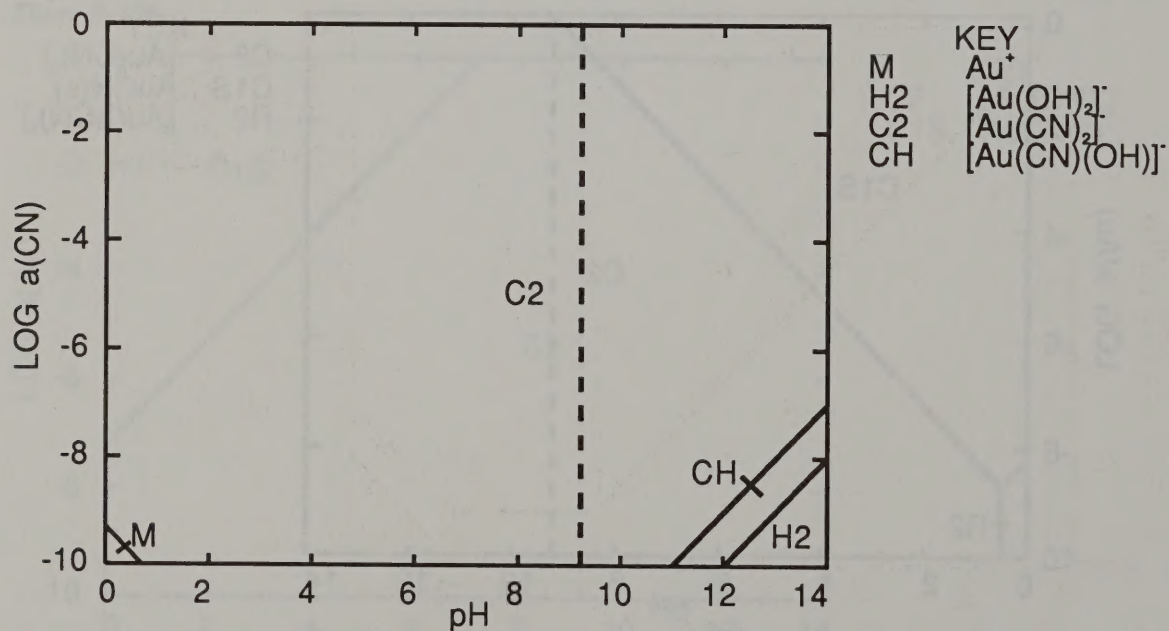


Figure E-127



$p\text{Au(I)}$ -pH diagram for  $p\text{CN} = 5.0$  and  $p\text{S}_2\text{O}_3 = 4.0$ .

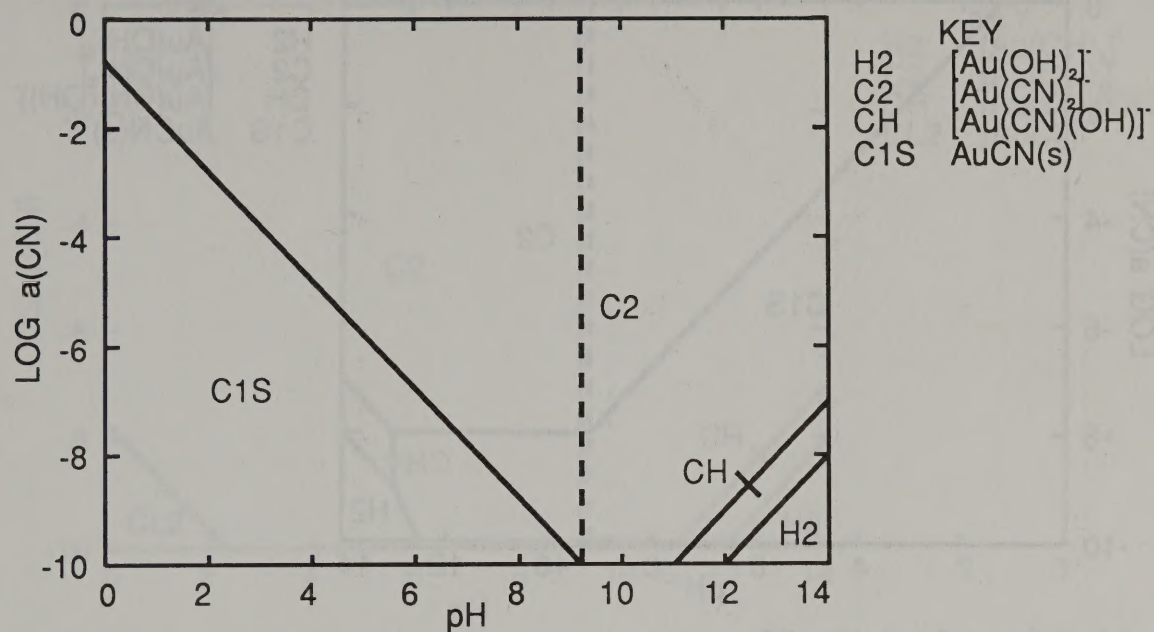
Figure E-128



$p\text{CN}$ -pH diagram for gold(I) solution species.

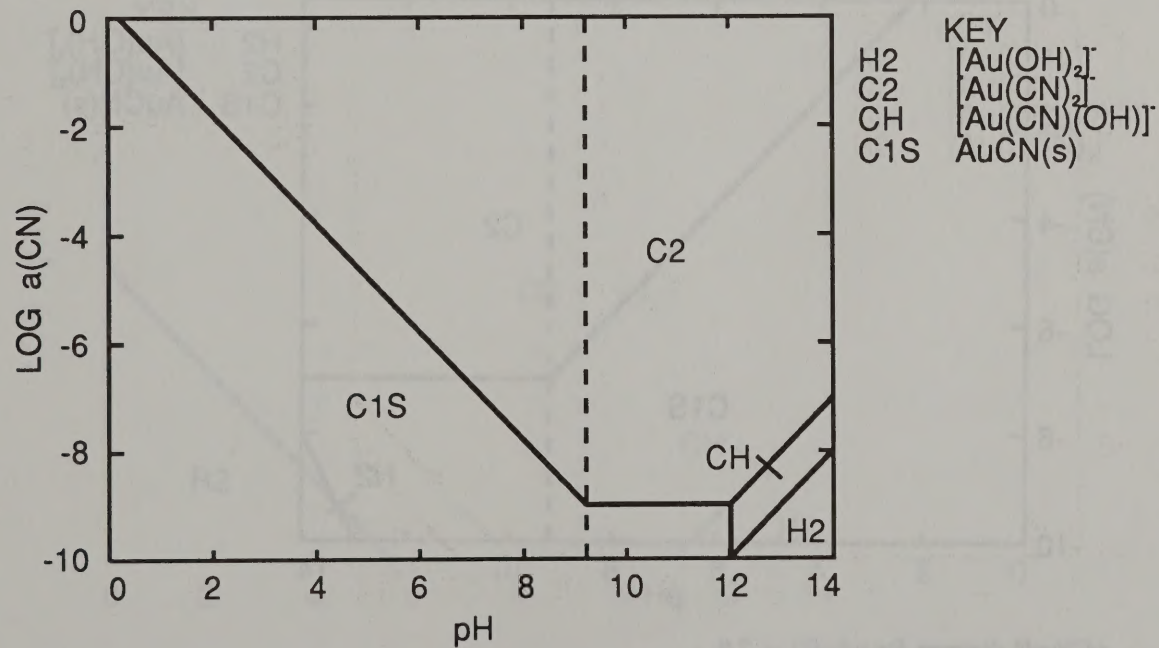


Figure E-129



*pCN-pH diagram for  $pAu(I) = 5.0$ .*

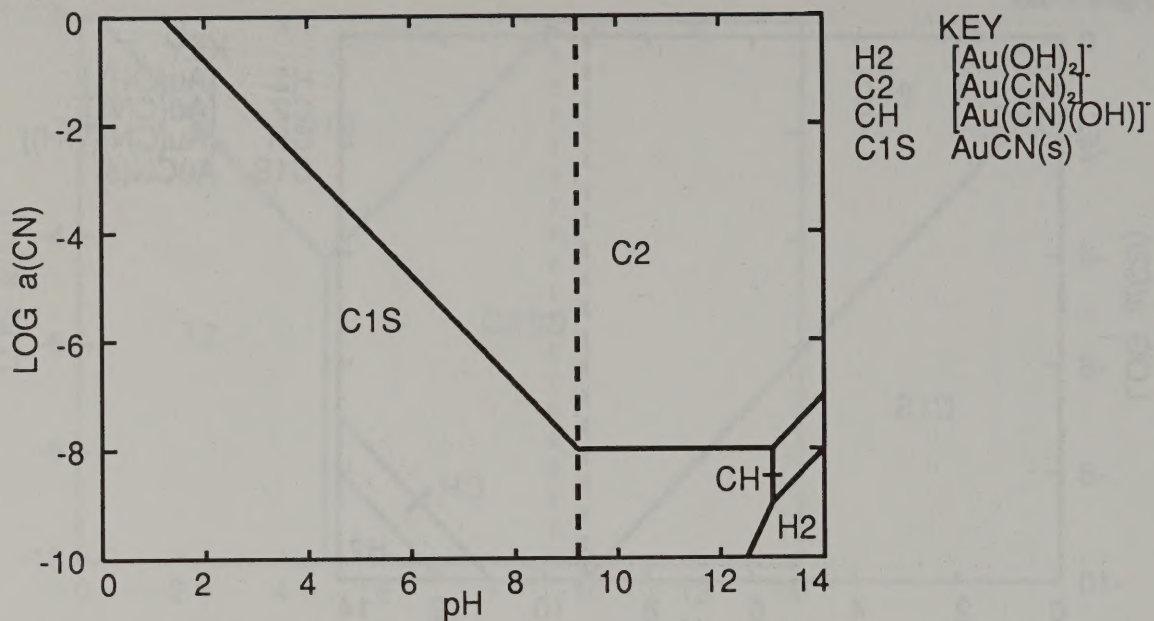
Figure E-130



*pCN-pH diagram for  $pAu(I) = 4.0$ .*

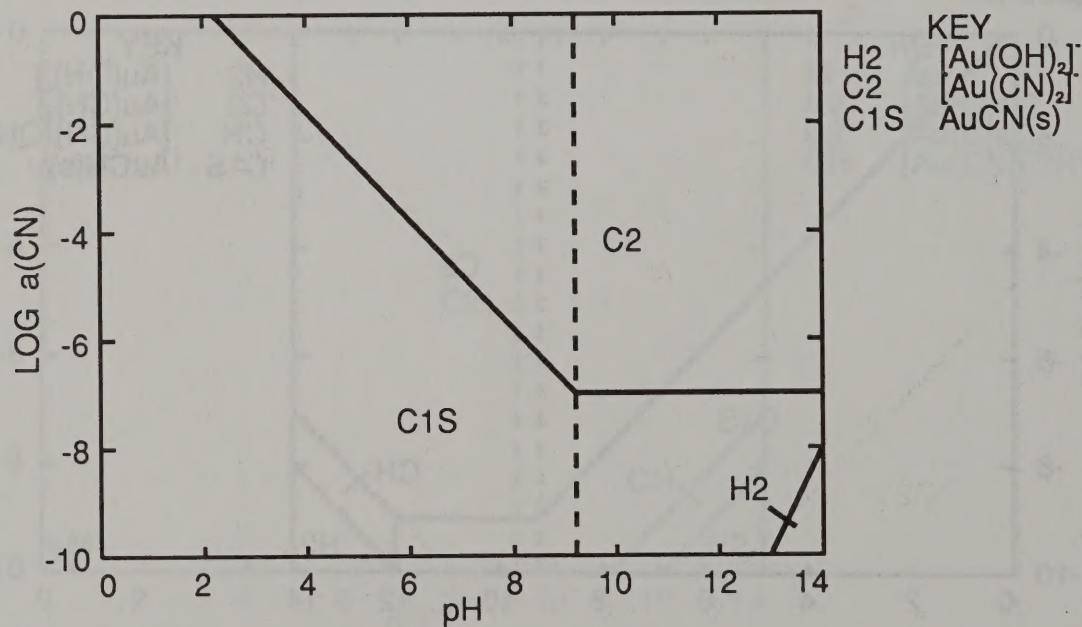


Figure E-131



$p\text{CN}$ - $\text{pH}$  diagram for  $p\text{Au(I)} = 3.0$ .

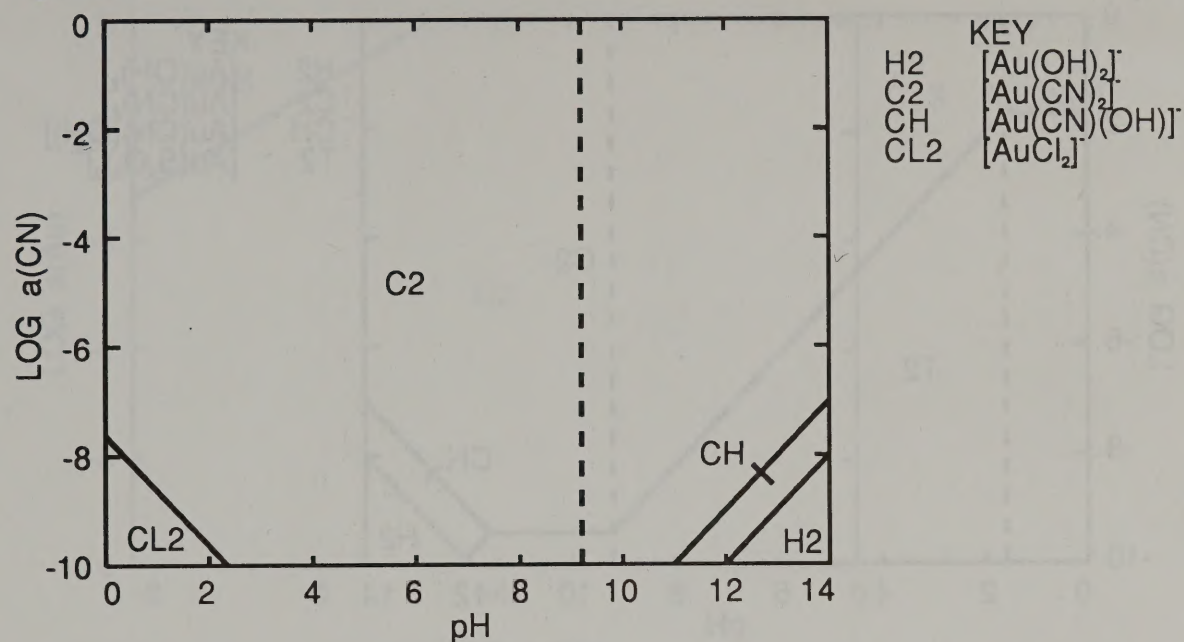
Figure E-132



$p\text{CN}$ - $\text{pH}$  diagram for  $p\text{Au(I)} = 2.0$ .

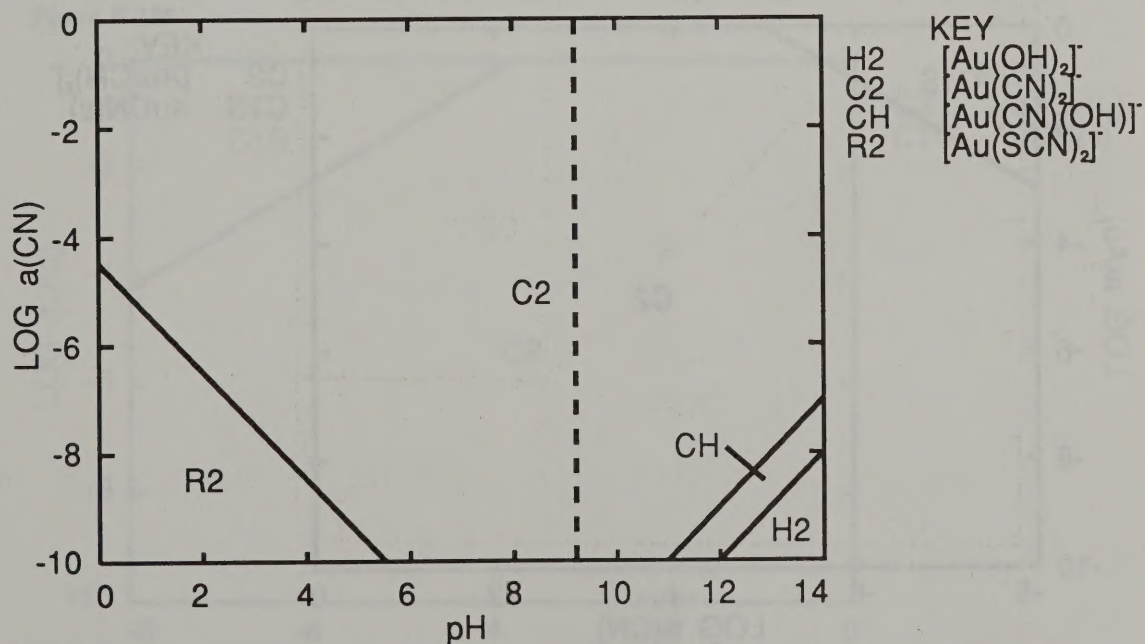


Figure E-133



*pCN-pH diagram for gold(I) solution species with  $p\text{Cl} = 3.0$ .*

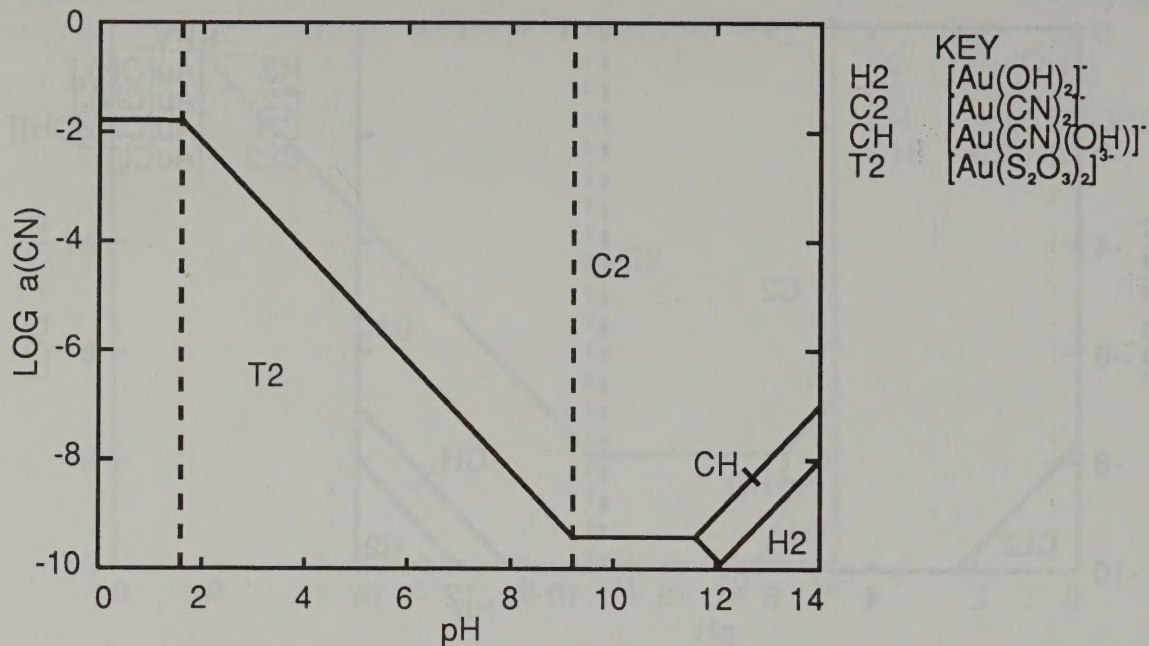
Figure E-134



*pCN-pH diagram for gold(I) solution species with  $p\text{SCN} = 4.0$ .*

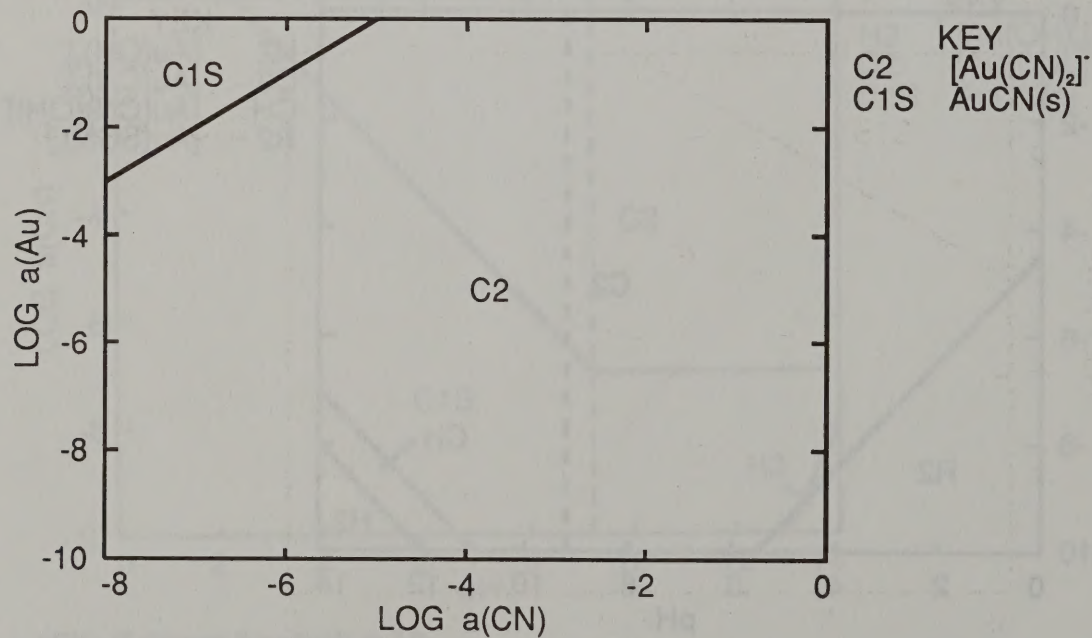


Figure E-135



*pCN-pH diagram for gold(I) solution species with  $pS_2O_3 = 4.0$ .*

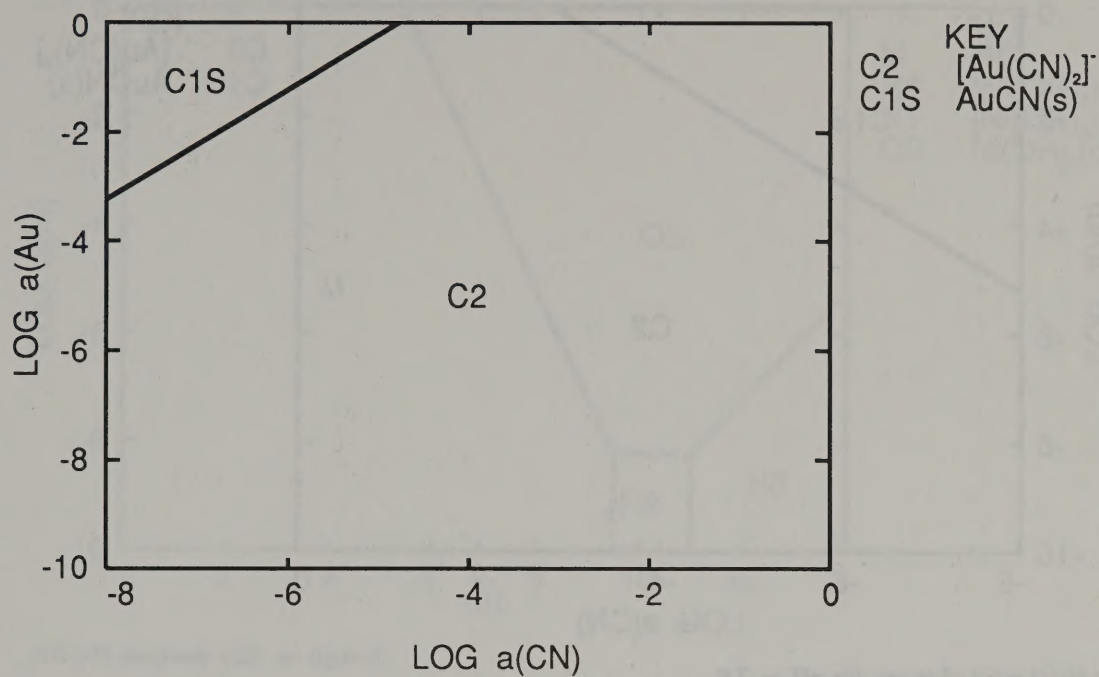
Figure E-136



*pAu(I)-pCN diagram for  $\text{pH} = 11.0$ .*

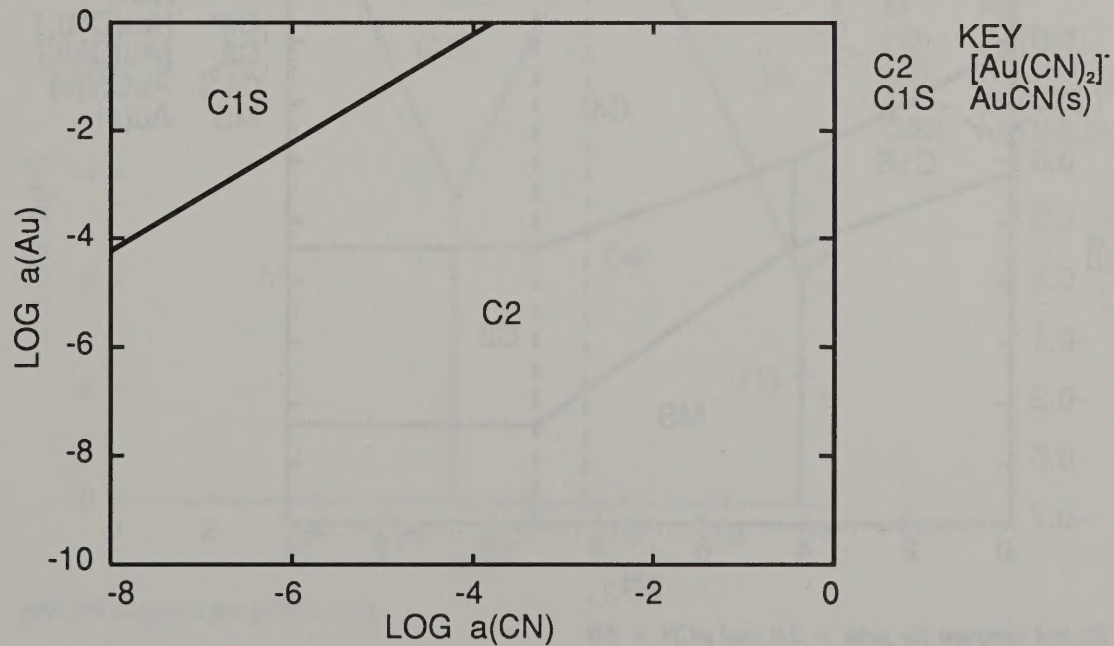


Figure E-137



$p\text{Au(I)}-p\text{CN}$  diagram for  $\text{pH} = 9.0$ .

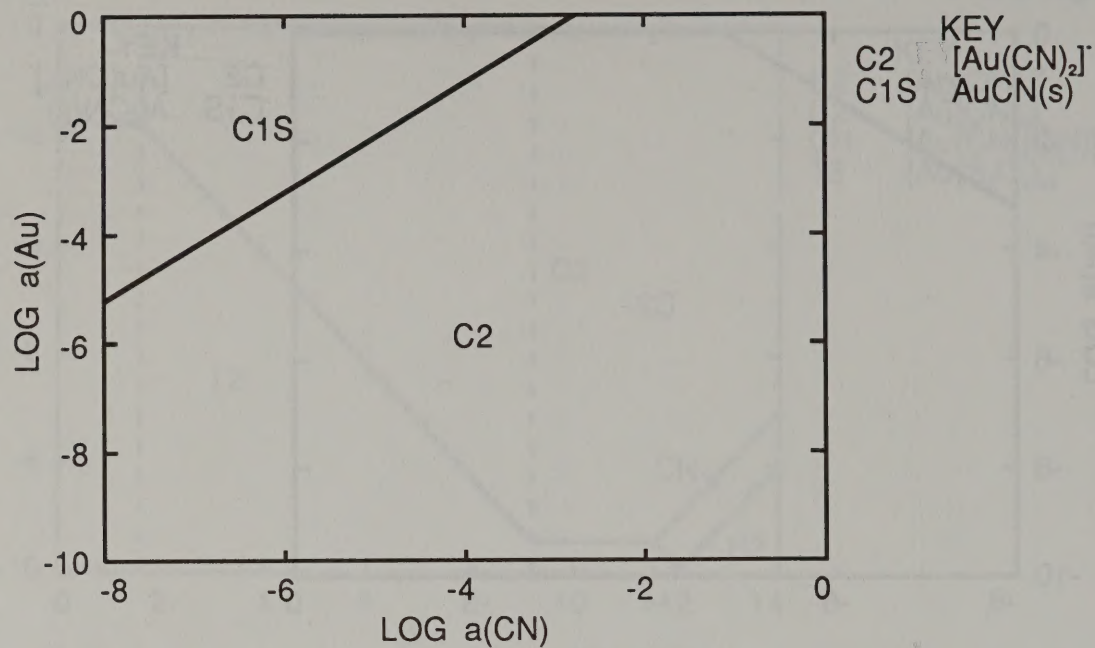
Figure E-138



$p\text{Au(I)}-p\text{CN}$  diagram for  $\text{pH} = 8.0$ .

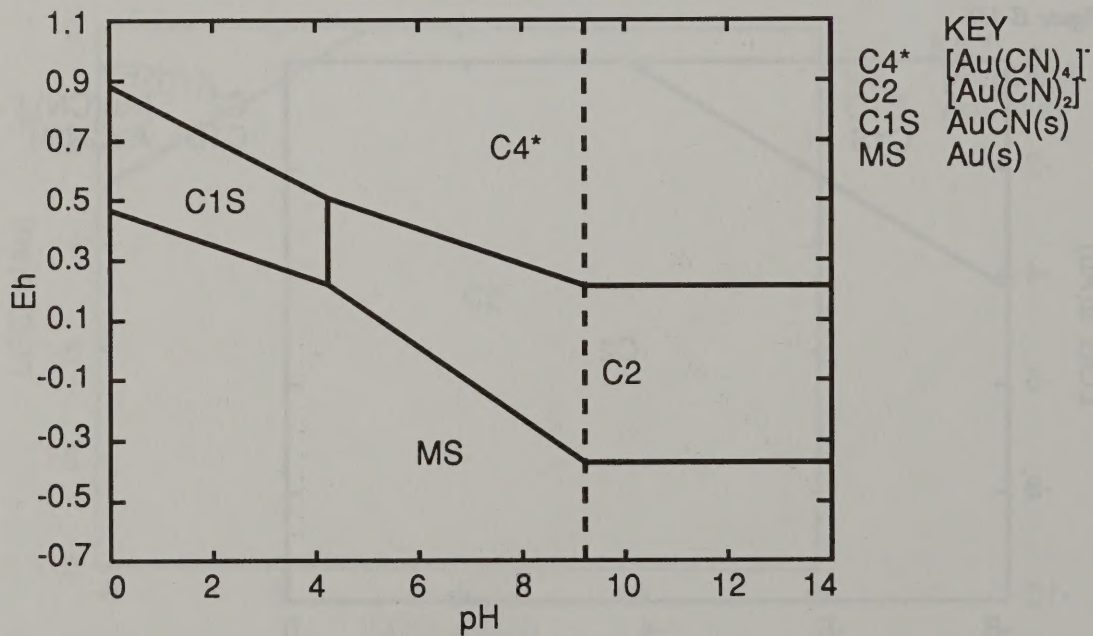


Figure E-139



$p\text{Au(I)}-p\text{CN}$  diagram for  $\text{pH} = 7.0$ .

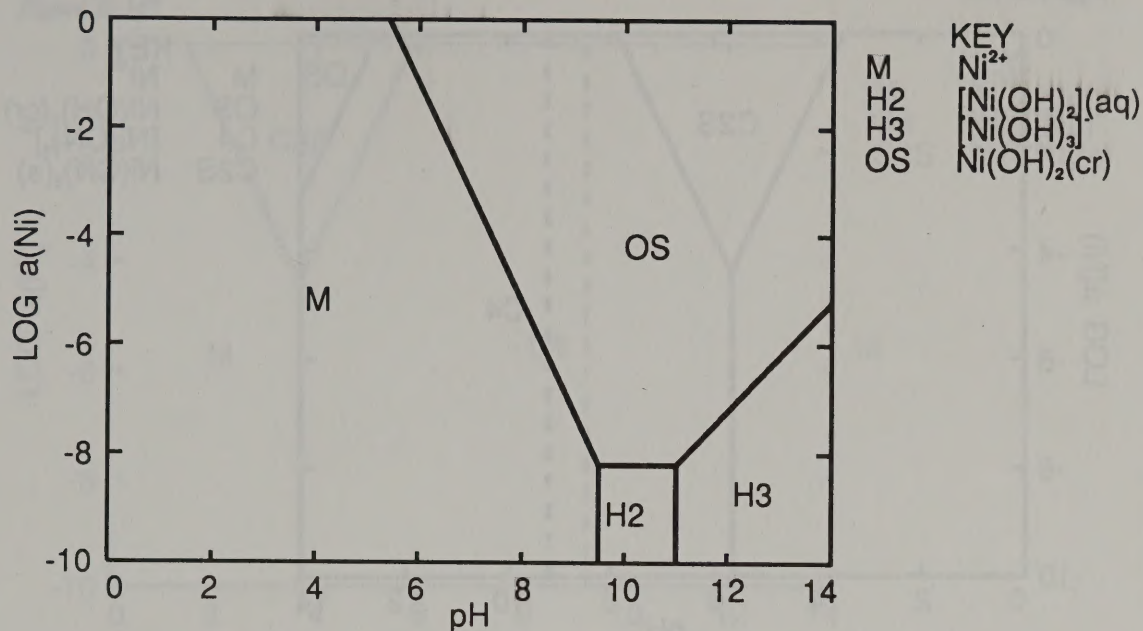
Figure E-140



$\text{Eh-pH}$  diagram for  $p\text{Au} = 2.0$  and  $p\text{CN} = 2.0$ .

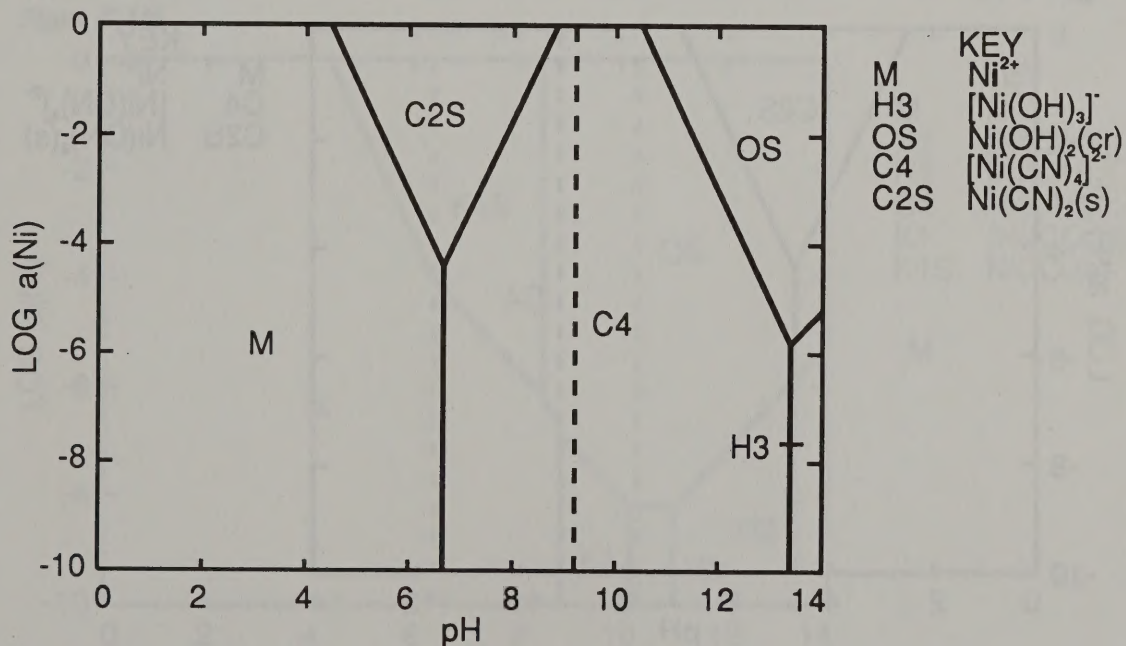


Figure E-141



*pNi-pH diagram with no ligands.*

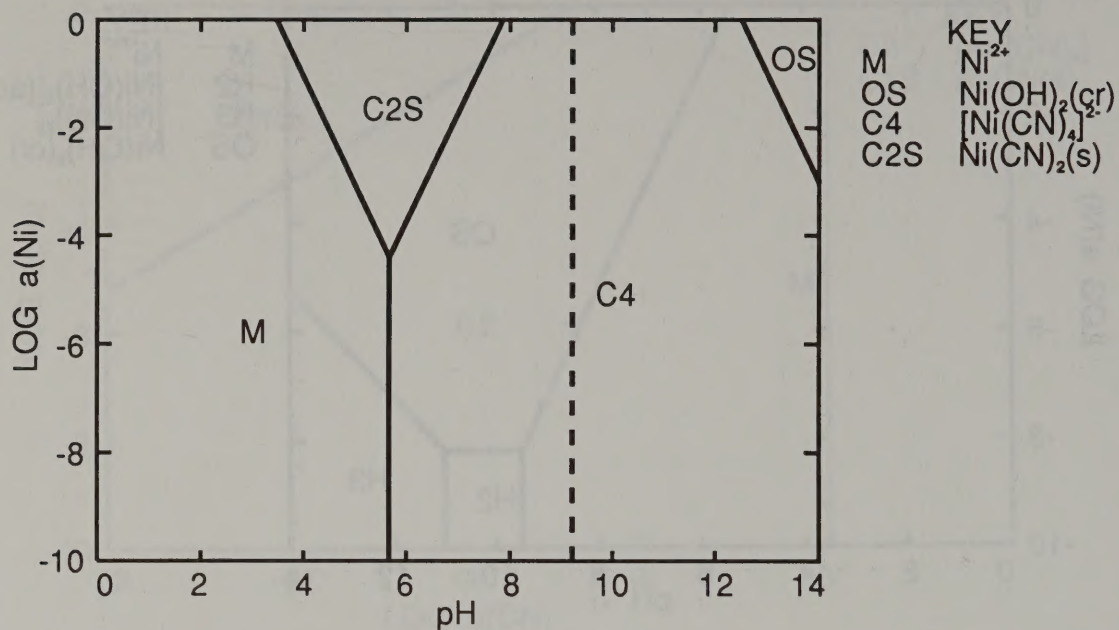
Figure E-142



*pNi-pH diagram for  $p\text{CN} = 5.0$ .*

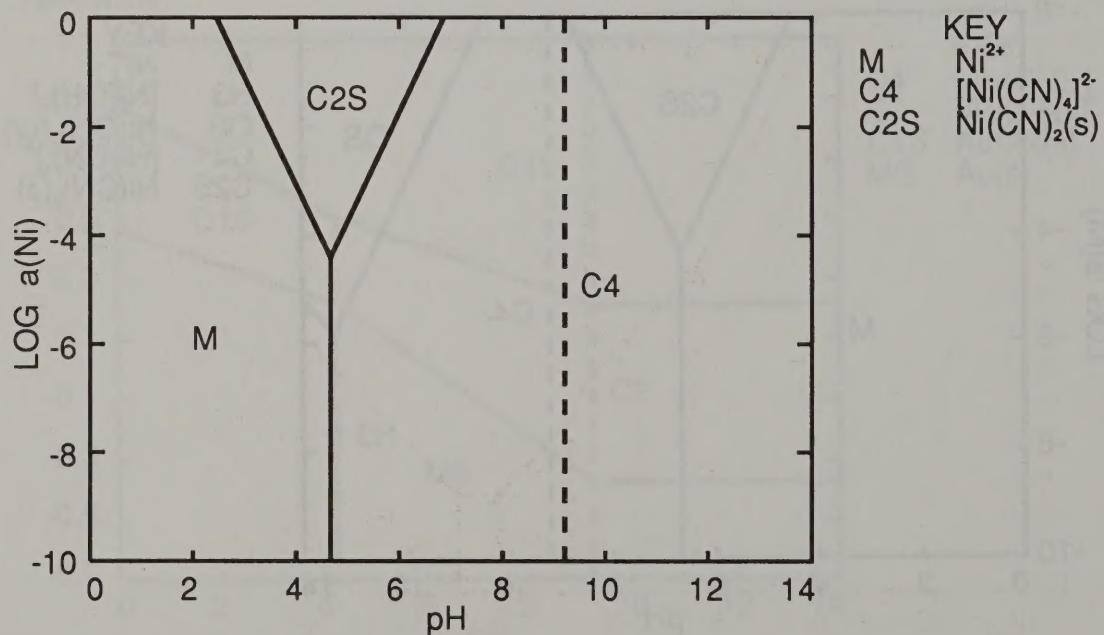


Figure E-143



$p\text{Ni}$ - $\text{pH}$  diagram for  $p\text{CN} = 4.0$ .

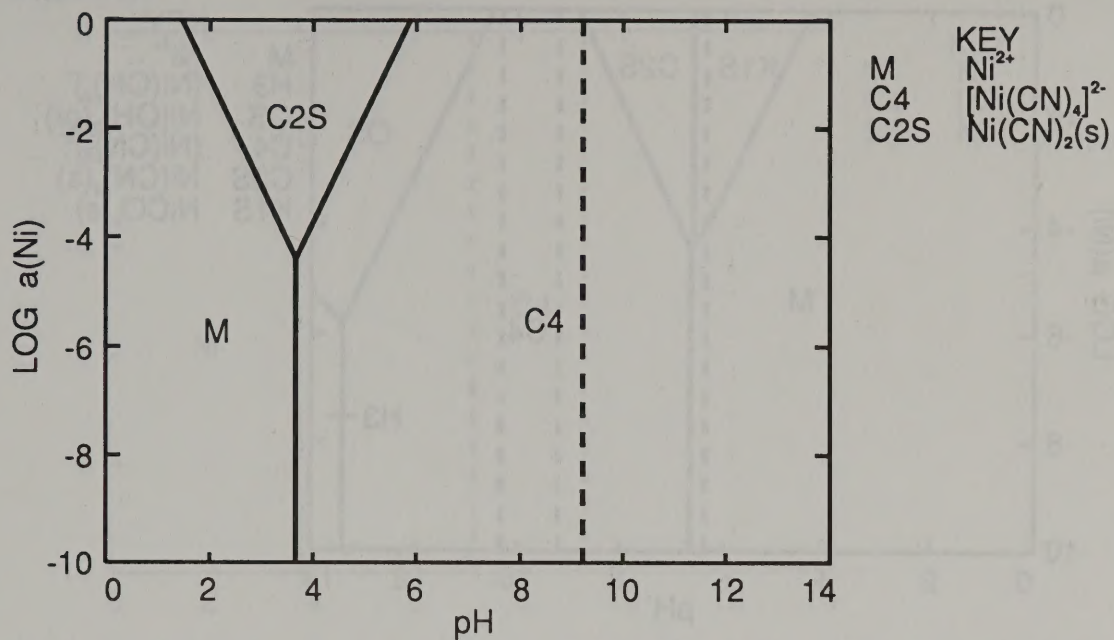
Figure E-144



$p\text{Ni}$ - $\text{pH}$  diagram for  $p\text{CN} = 3.0$ .

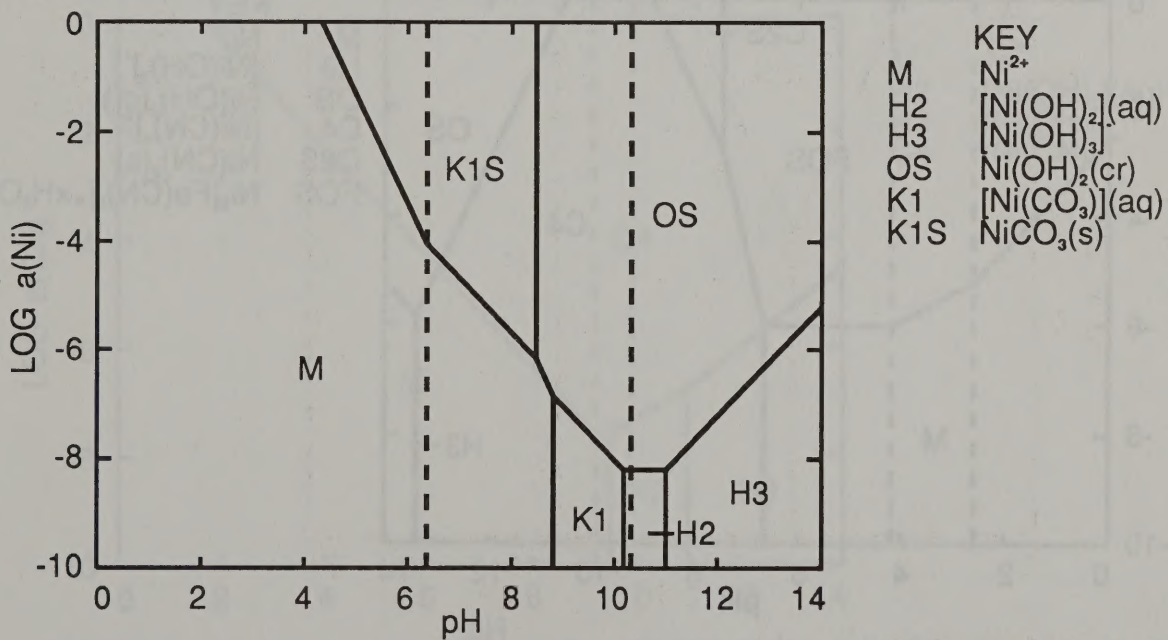


Figure E-145



*pNi-pH diagram for  $pCN = 2.0$ .*

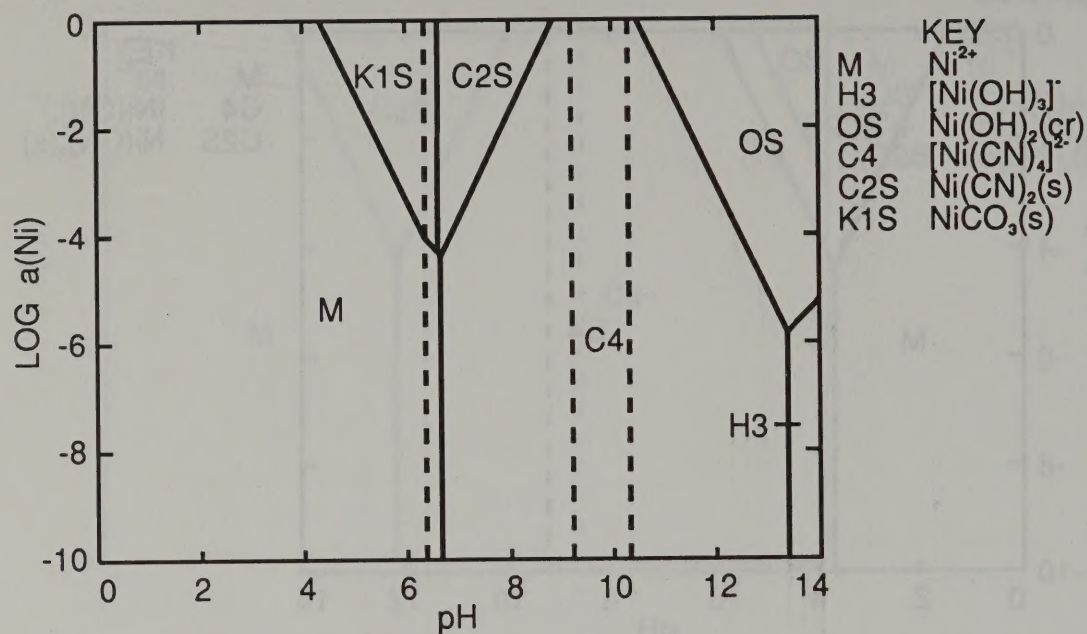
Figure E-146



*pNi-pH diagram for  $p\text{CO}_3 = 3.0$ .*

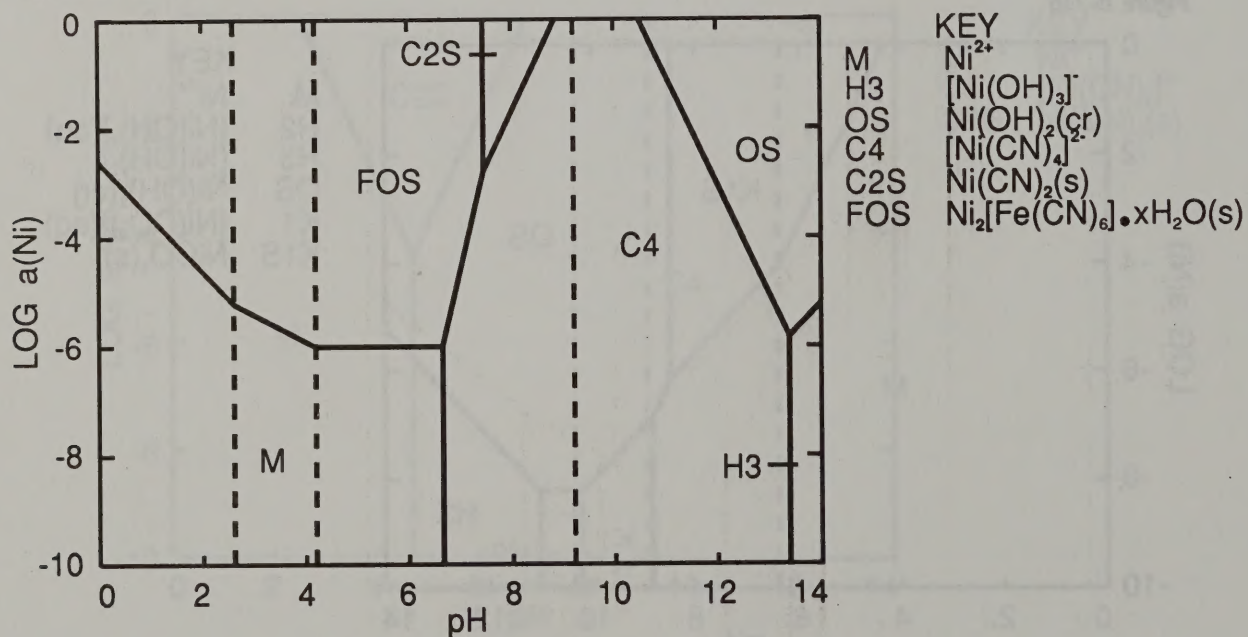


Figure E-147



*pNi-pH diagram for  $p\text{CN} = 5.0$  and  $p\text{CO}_3 = 3.0$ .*

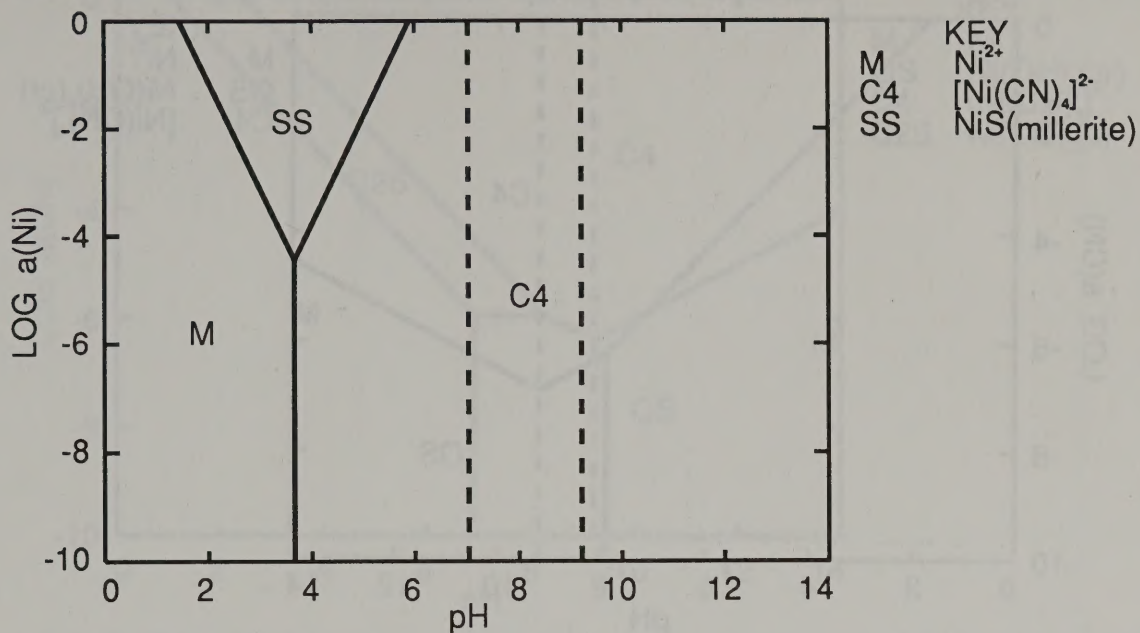
Figure E-148



*pNi-pH diagram for  $p\text{CN} = 5.0$  and  $p[\text{Fe}(\text{CN})_6^{4-}] = 4.0$ .*

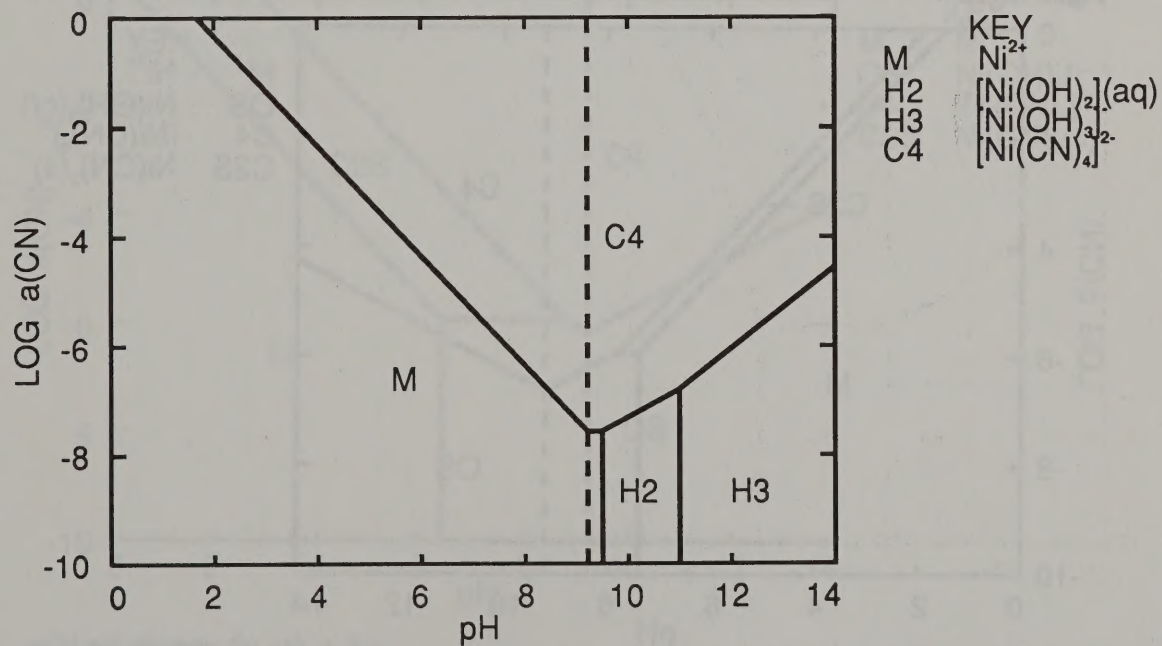


Figure E-149



*pNi-pH diagram for  $p\text{CN} = 2.0$  and  $p\text{S} = 6.0$ .*

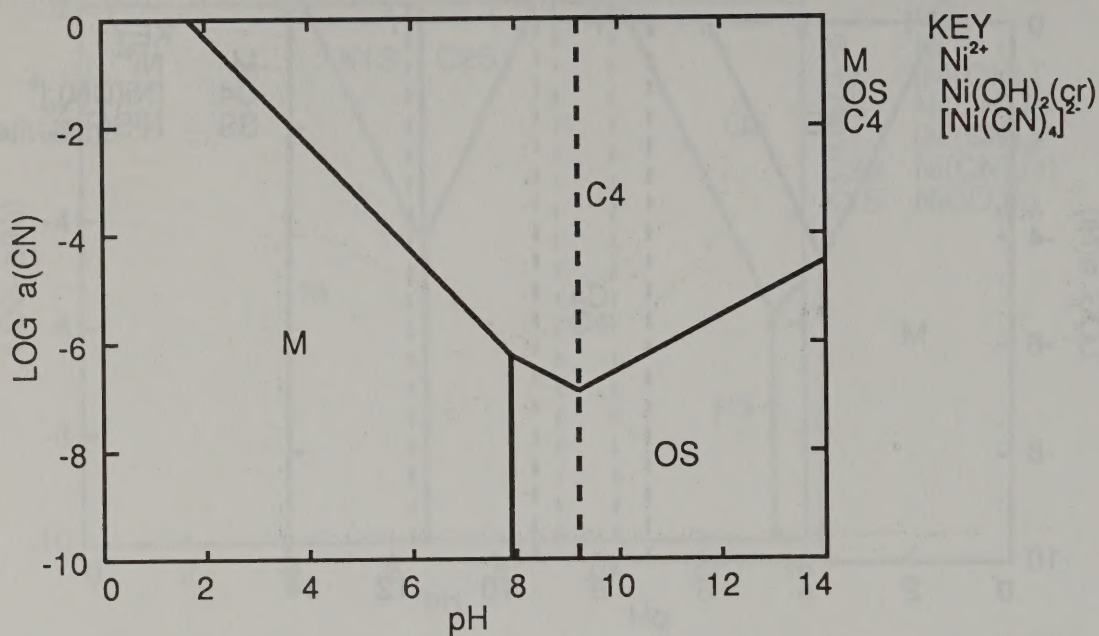
Figure E-150



*pCN-pH diagram for nickel solution species.*

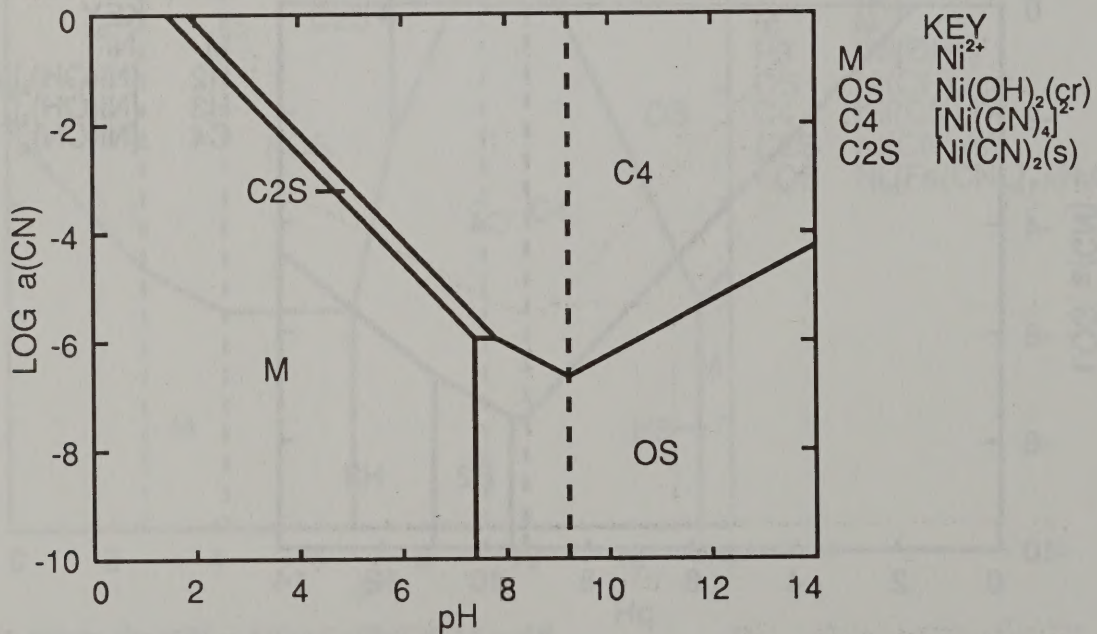


Figure E-151



*pCN-pH diagram for  $p\text{Ni} = 5.0$ .*

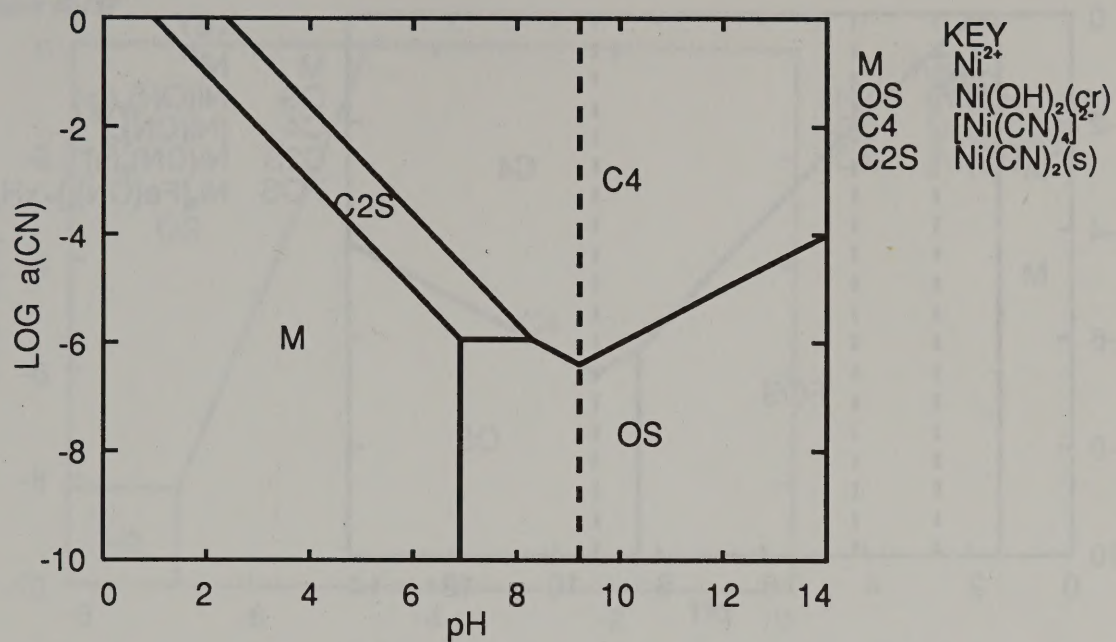
Figure E-152



*pCN-pH diagram for  $p\text{Ni} = 4.0$ .*

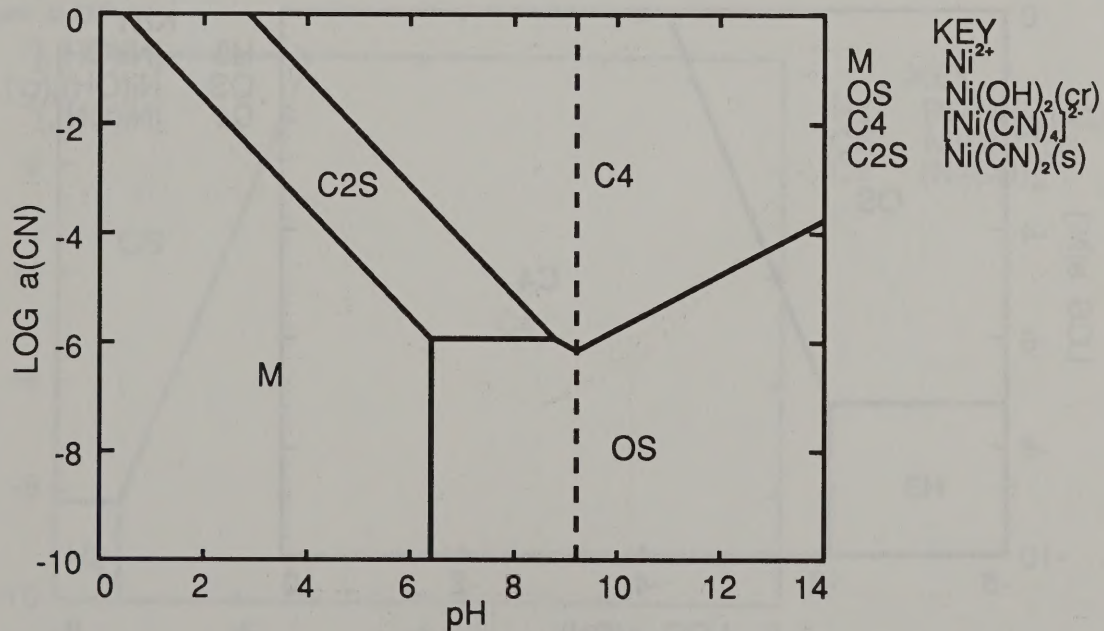


Figure E-153



pCN-pH diagram for  $pNi = 3.0$ .

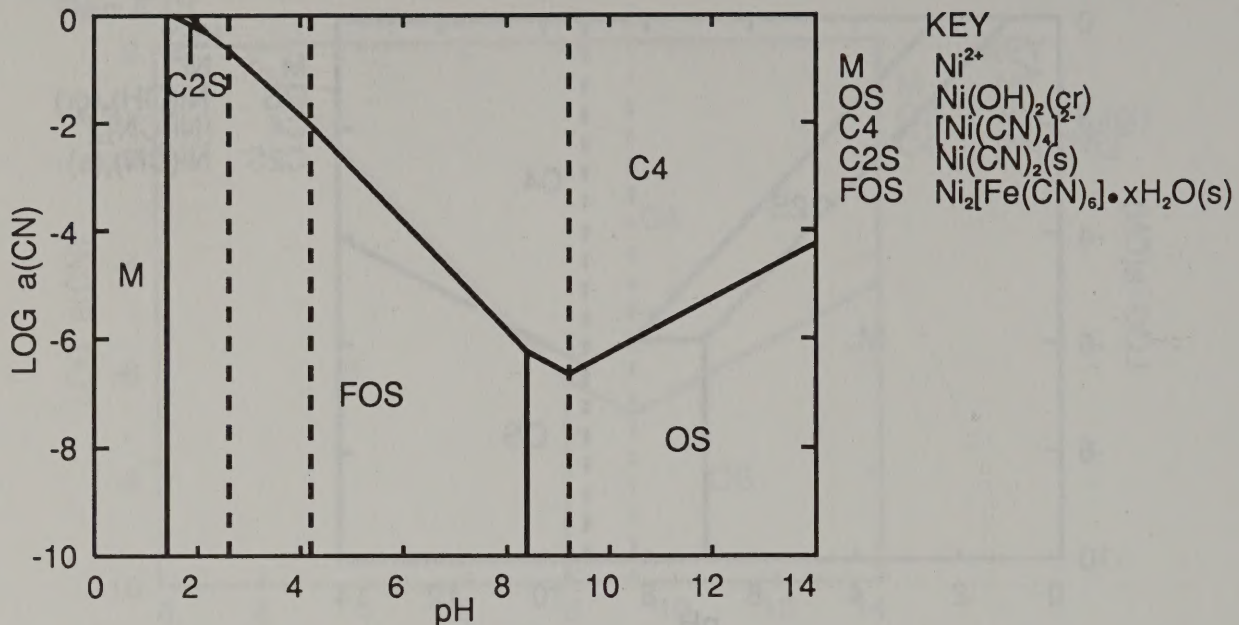
Figure E-154



pCN-pH diagram for  $pNi = 2.0$ .

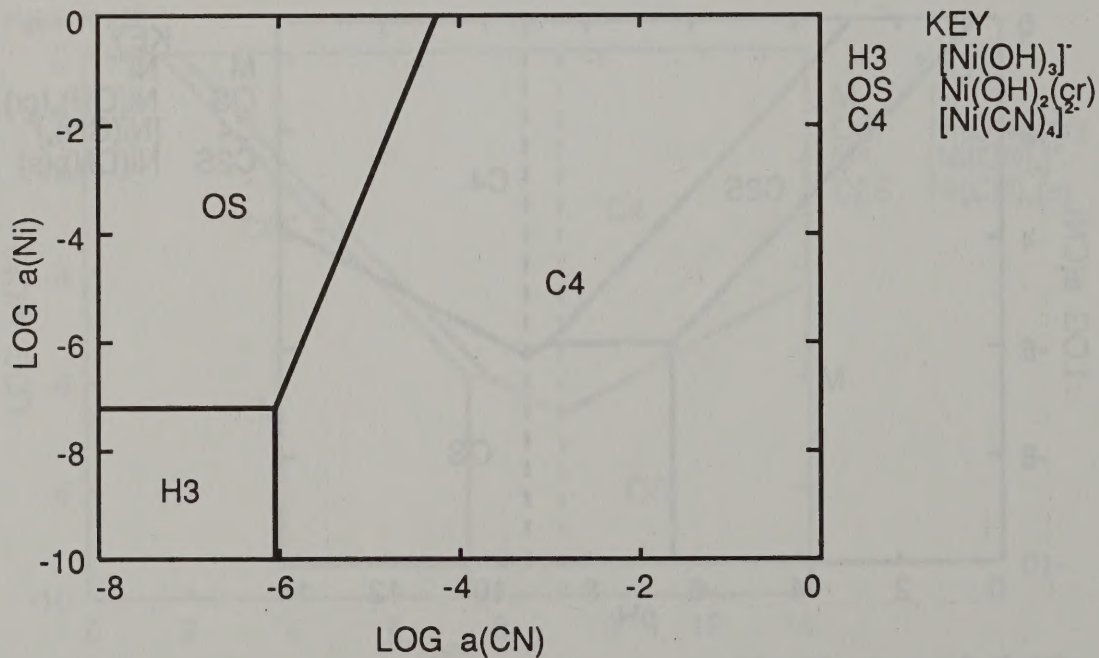


Figure E-155



*pCN-pH diagram for  $p\text{Ni} = 4.0$  and  $p[\text{Fe}(\text{CN})_6^{4-}] = 4.0$ .*

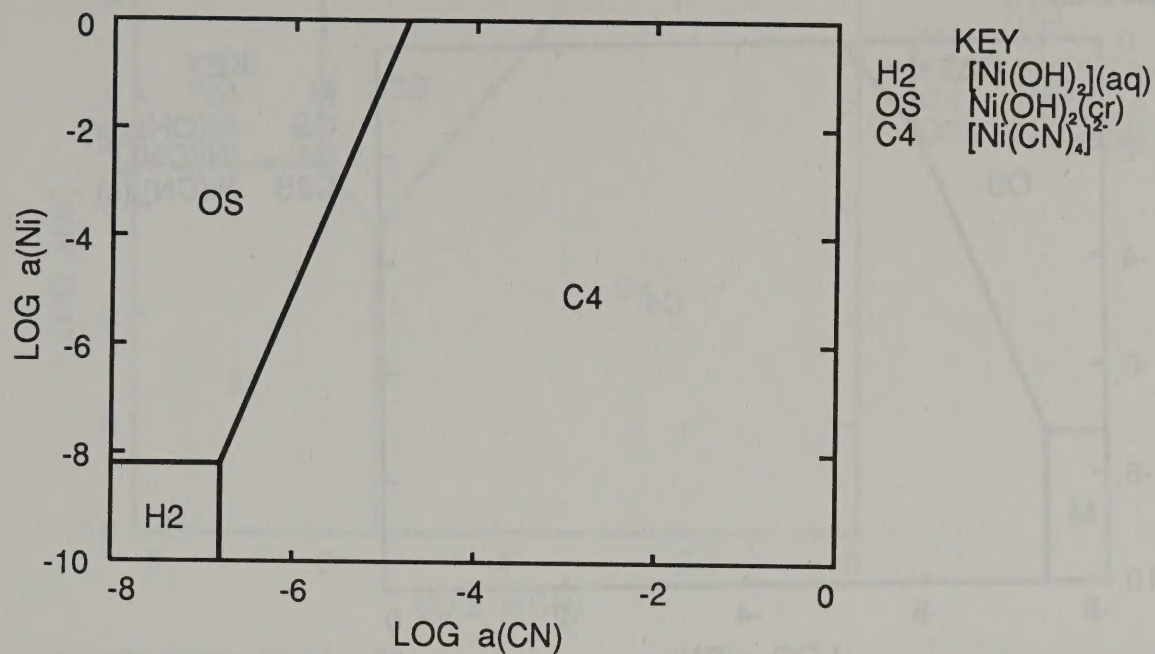
Figure E-156



*pNi-pCN diagram for  $\text{pH} = 12.0$ .*

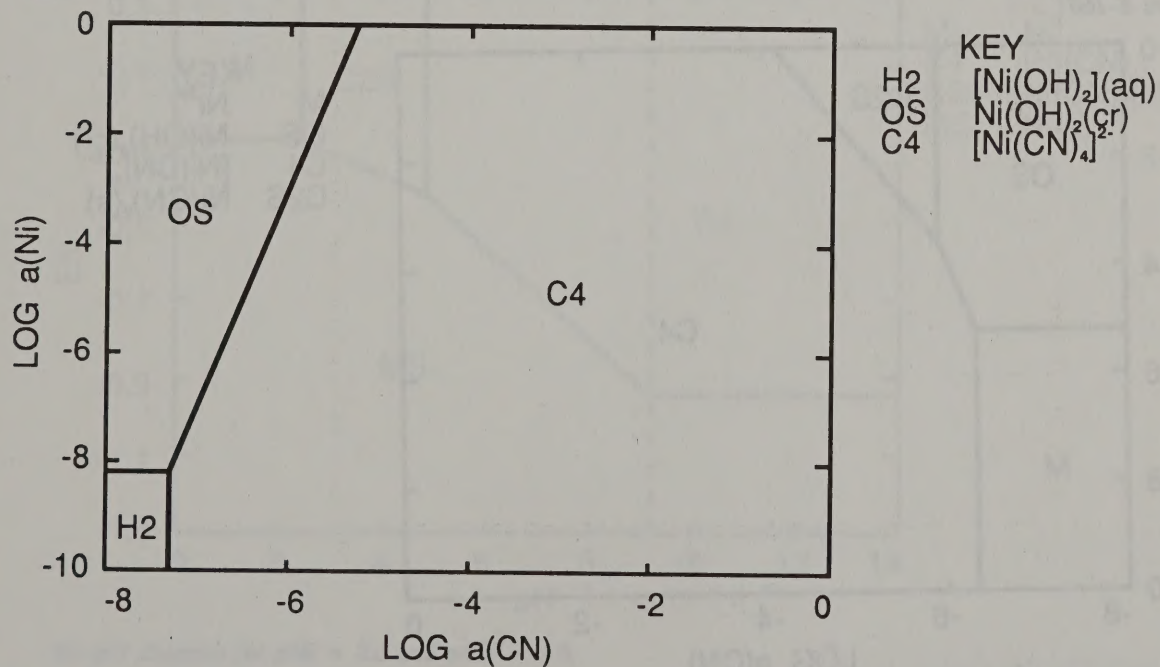


Figure E-157



pNi-pCN diagram for pH = 11.0.

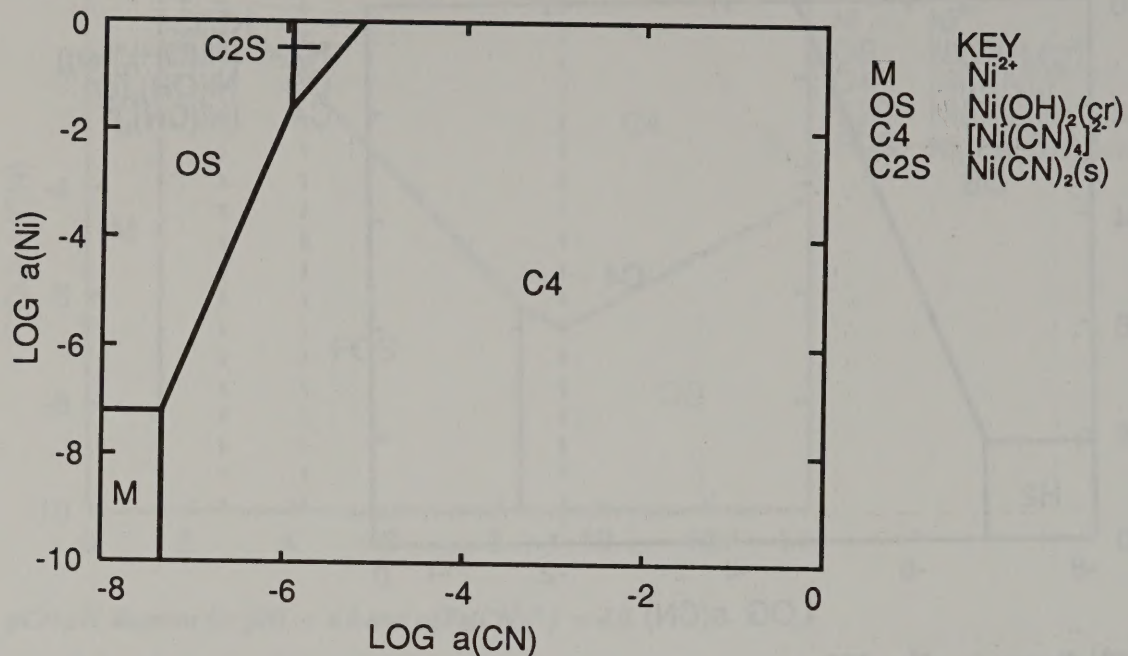
Figure E-158



pNi-pCN diagram for pH = 10.0.

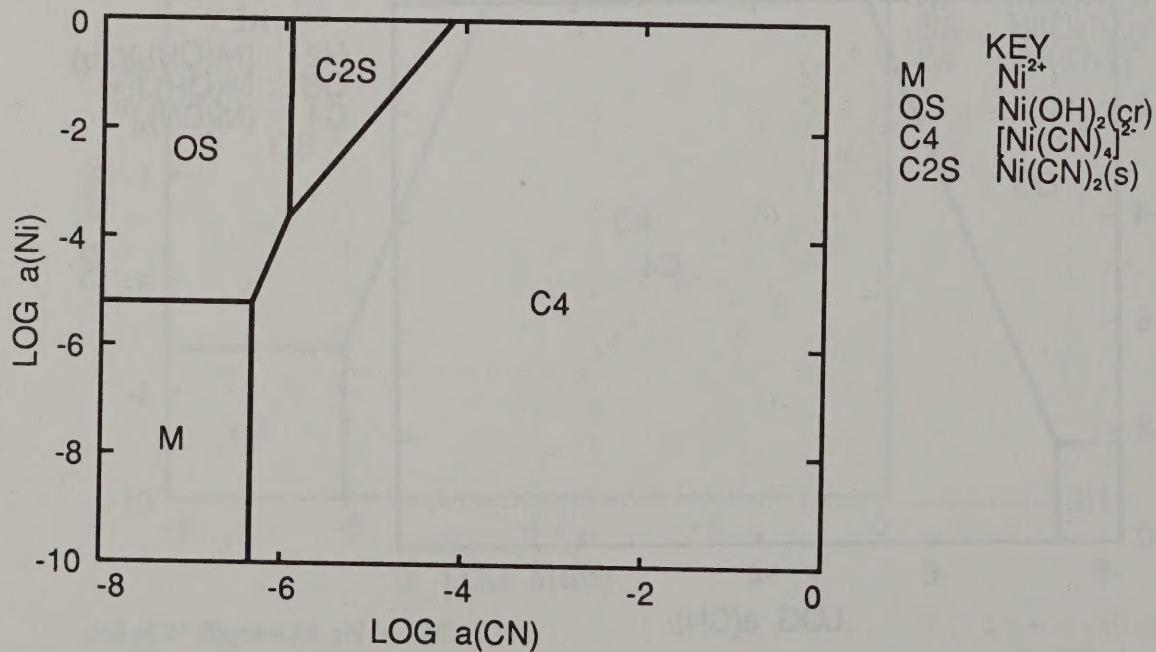


Figure E-159



pNi-pCN diagram for pH = 9.0.

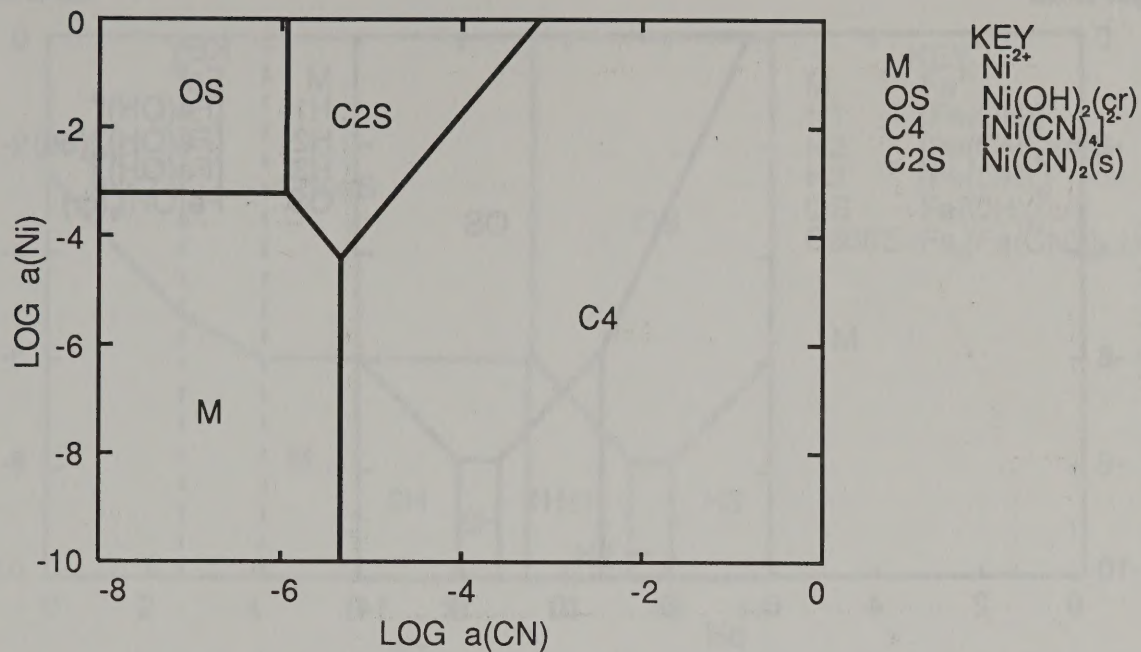
Figure E-160



pNi-pCN diagram for pH = 8.0.

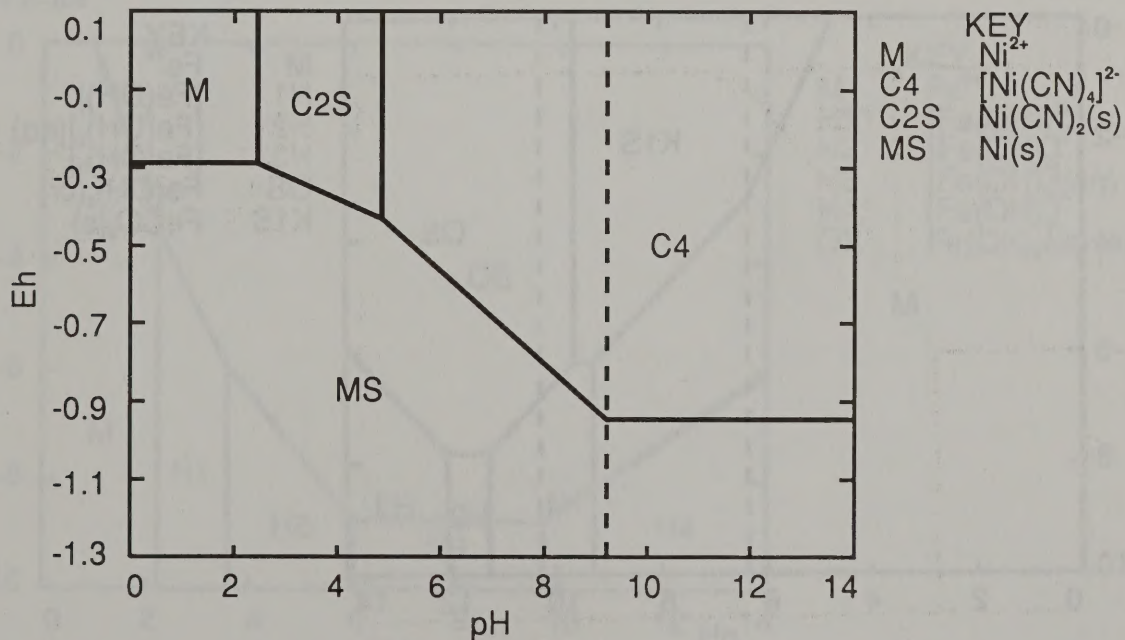


Figure E-161



*pNi-pCN diagram for  $\text{pH} = 7.0$ .*

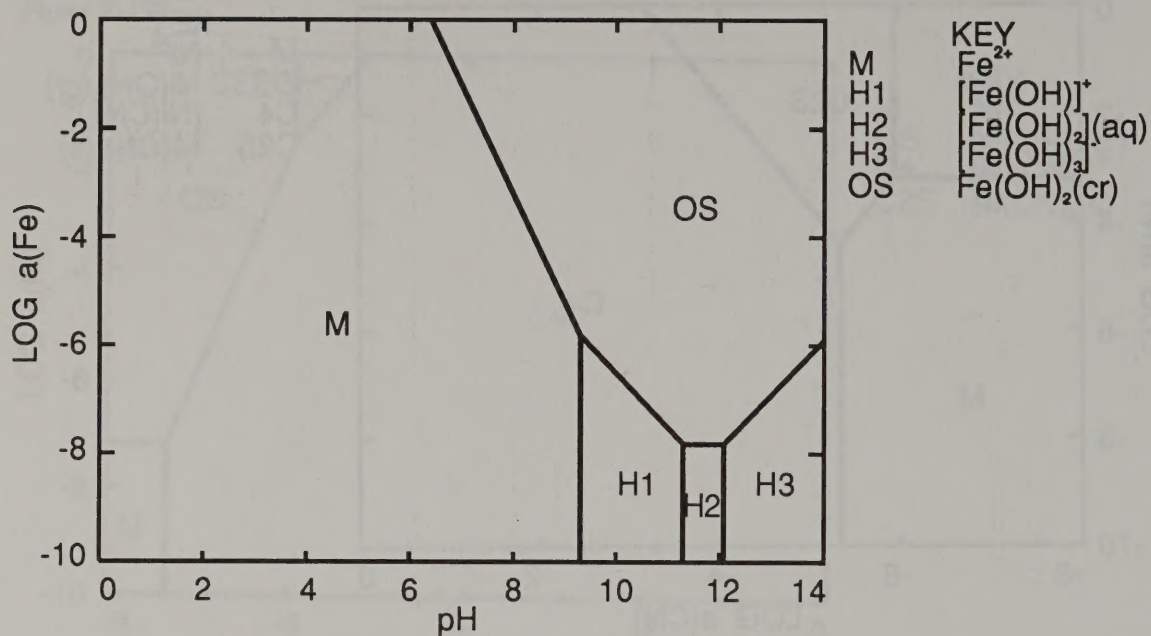
Figure E-162



*Eh-pH diagram for  $\text{pNi} = 2.0$  and  $\text{pCN} = 2.0$ .*

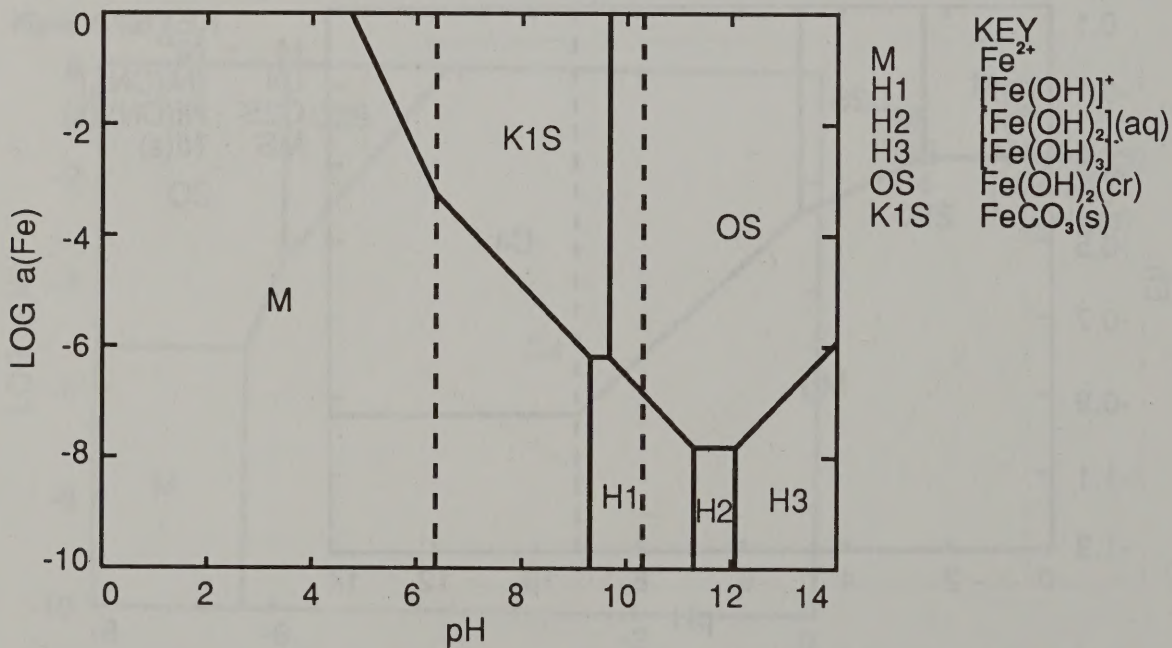


Figure E-163



*pFe(II)-pH diagram with no ligands.*

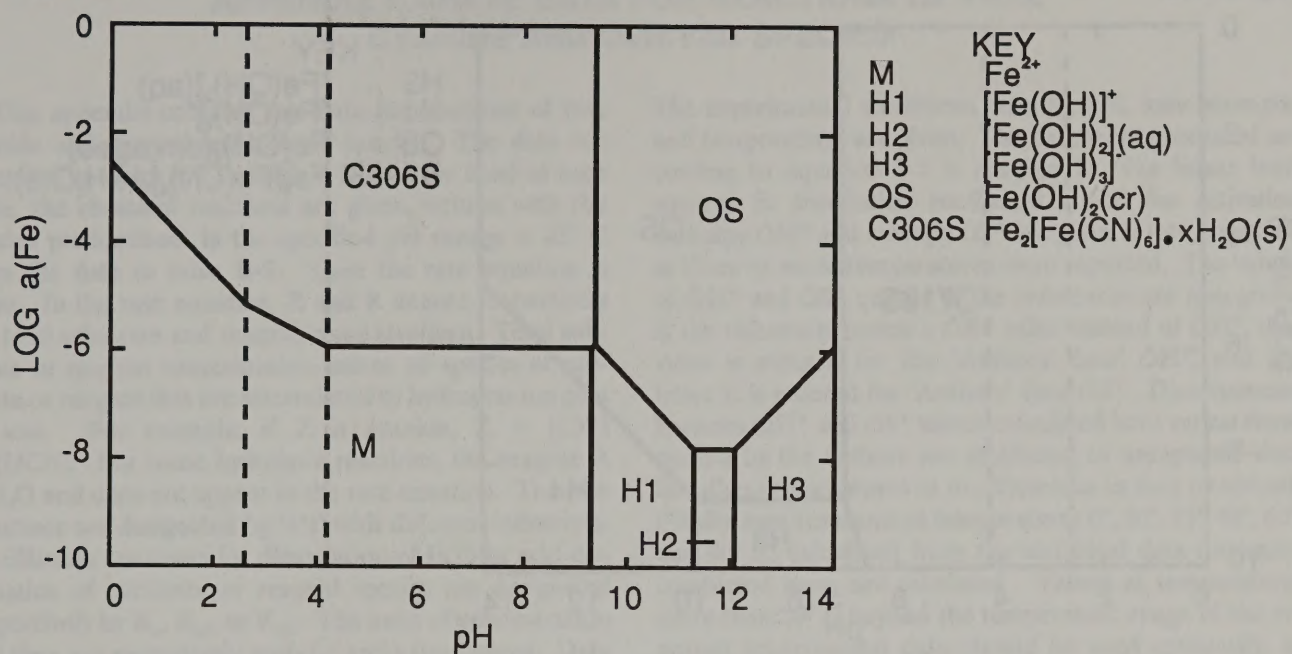
Figure E-164



*pFe(II)-pH diagram for  $p\text{CO}_3 = 3.0$ .*

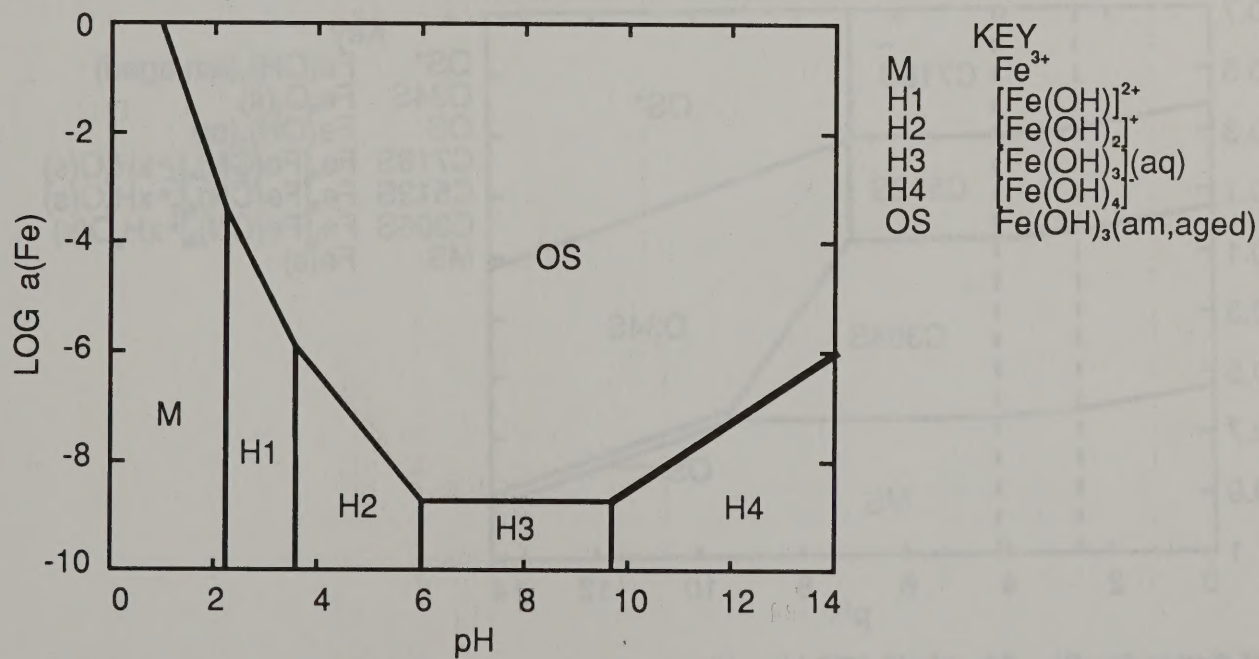


Figure E-165



$p\text{Fe(II)}$ - $\text{pH}$  diagram for  $p[\text{Fe}(\text{CN})_6^{4-}] = 4.0$ .

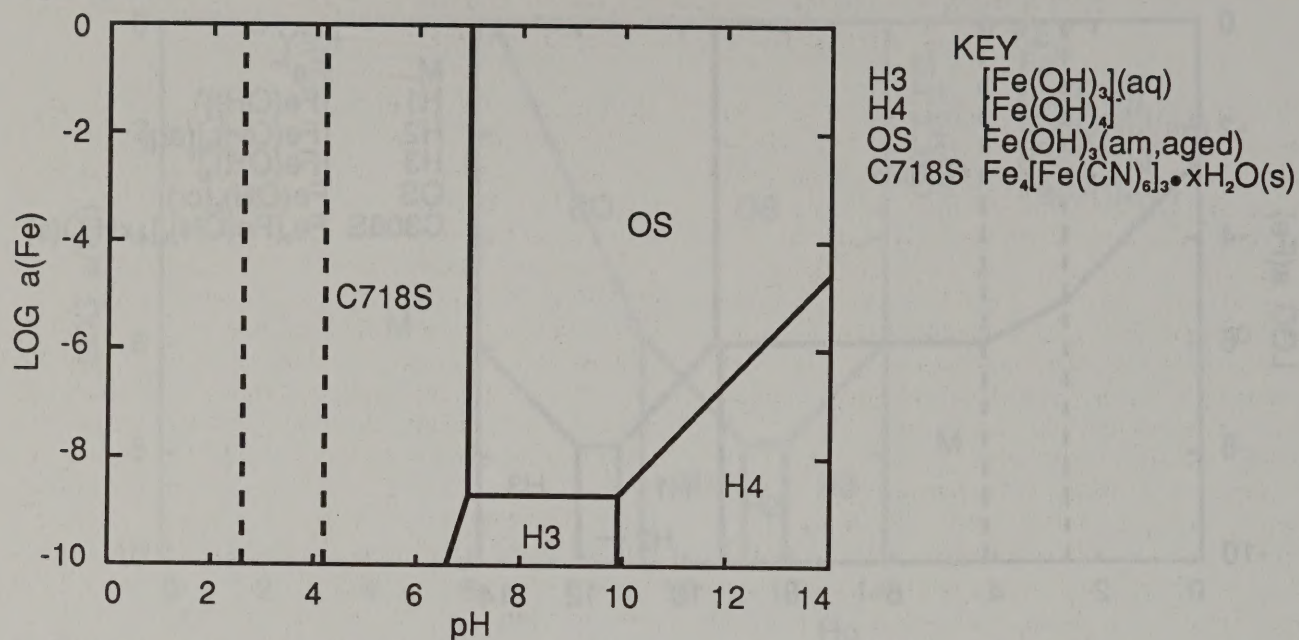
Figure E-166



$p\text{Fe(III)}$ - $\text{pH}$  diagram with no ligands.

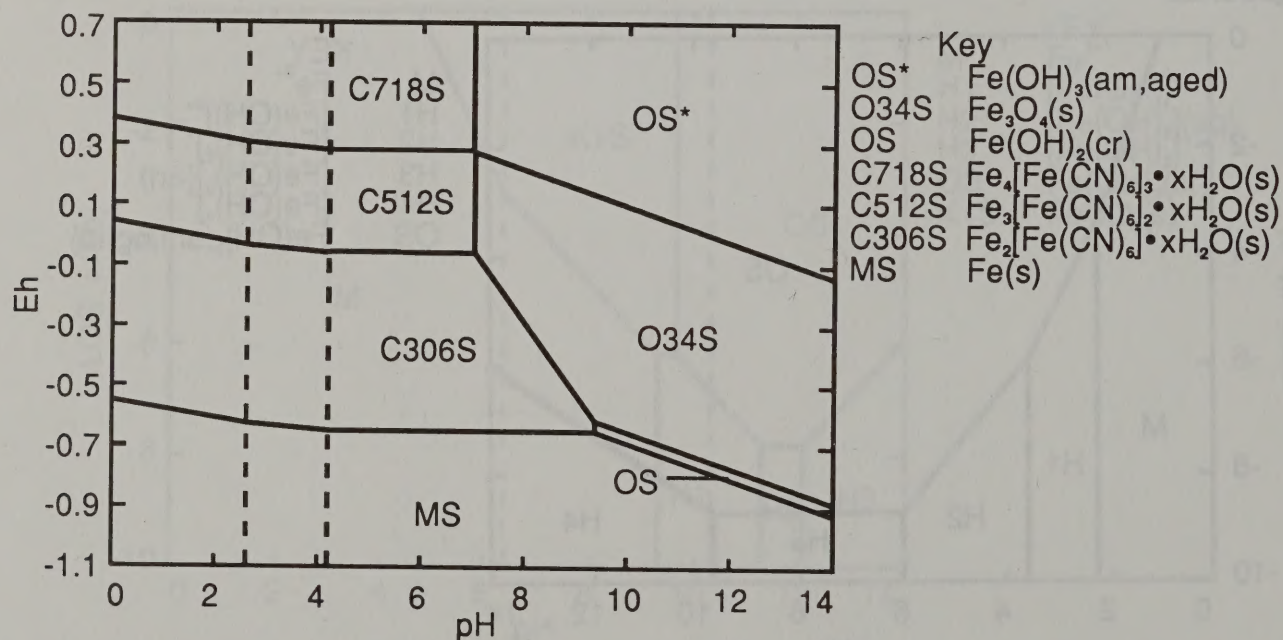


Figure E-167



$p\text{Fe(III)}\text{-pH diagram for } p[\text{Fe}(\text{CN})_6^{4-}] = 4.0.$

Figure E-168



$\text{Eh-pH diagram for } p\text{Fe} = 2.0 \text{ and } p[\text{Fe}(\text{CN})_6^{4-}] = 4.0.$



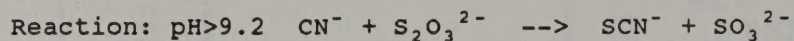
## APPENDIX F.—RATE DATA FOR REACTIONS OF FREE CYANIDE AND DERIVED SPECIES

This appendix contains rate data for reactions of free cyanide and derived and related species. The data are compiled in tables F-1 through F-16. At the head of each table, the chemical reactions are given, written with the species predominant in the specified pH ranges at 25° C from the data in table B-2. Then the rate equation is given. In the rate equation, Z and R denote respectively the total substrate and reagent concentrations. Total substrate or reagent concentration means all species of substrate or reagent that are interrelated by hydrogen-ion gain or loss. For example, if Z is cyanide,  $Z = [\text{CN}^-] + [\text{HCN}]$ . For some hydrolysis reactions, the reagent R is  $\text{H}_2\text{O}$  and does not appear in the rate equation. The rate constants are designated by "k's" with different subscripts. Equilibrium constants for dissociation of  $\text{H}_2\text{O}$  or acid dissociation of substrate or reagent species are designated respectively by  $K_w$ ,  $K_{a2}$ , or  $K_{aR}$ . The units of concentration and time are respectively  $\text{mol} \cdot \text{L}^{-1}$  and s throughout. Data are tabulated for each rate constant in the rate equation. The cited references are listed at the end of chapter 7.

The experimental conditions, namely, pH, ionic strength, and temperature, are given. The data were processed according to equation 7-7 in chapter 7. The linear least squares fit correlation coefficient  $r$  and the activation enthalpy  $\Delta H^*$  and entropy  $\Delta S^*$  are given if rate constants at three or more temperatures were reported. The values of  $\Delta H^*$  and  $\Delta S^*$  quoted in the references are also given. If the reference quotes a  $\Delta E^*$  value instead of  $\Delta H^*$ , that value is entered for the "Authors' data"  $\Delta H^*$ , and the letter E is entered for "Authors' data"  $\Delta S^*$ . Discrepancies between  $\Delta H^*$  and  $\Delta S^*$  values calculated here versus those quoted by the authors are attributed to unreported data for other temperatures or to differences in data treatment. Finally, rate constants at temperatures 0°, 10°, 25°, 40°, 60°, and 90° C, calculated from the statistical data treatment conducted here, are tabulated. Values at temperatures more than 20° C beyond the temperature range of the reported experimental data should be used cautiously, as indicated by the tabulated standard errors.



Table F-1.-Kinetic data for reaction of cyanide with thiosulfate



Rate equation:  $-\text{R}^{-1}\text{Z}^{-1}\text{dZ}/\text{dt} = k_1 K_a (K_a + [\text{H}^+])^{-1}$

Reported rate constants	$k_1$	$k_1$
Reference	28	28
pH range	<sup>1</sup> 11	<sup>1</sup> 11
Ionic strength, <u>M</u>	0	0.09
Temperature, °C	25-90	25-90
Statistical processing		
Number of points	3	3
Correlation coefficient	0.9986	0.9959
$\Delta H^\circ$ , kJ	43.8	39.1
	$\pm 2.3$	$\pm 3.5$
$\Delta S^\circ$ , J·K	-192.5	-198.5
	$\pm 7.0$	$\pm 10.7$
Authors' data		
$\Delta H^\circ$ or $\Delta E^\circ$ , kJ	51.9	N
	$\pm 1.7$	
$\Delta S^\circ$ , J·K	-163.2	N
	$\pm 12.6$	
Calculated rate constants		
0° C	(2.1 $\pm$ 0.5) E-6	(8.1 $\pm$ 2.8) E-6
10	(4.4 $\pm$ 0.8) E-6	(1.55 $\pm$ 4.4) E-5
25	(1.17 $\pm$ 1.5) E-5	(3.8 $\pm$ 0.8) E-5
40	(2.9 $\pm$ 0.3) E-5	(8.4 $\pm$ 1.2) E-5
60	(8.4 $\pm$ 0.6) E-5	(2.2 $\pm$ 0.3) E-4
90	(3.4 $\pm$ 0.4) E-4	(7.7 $\pm$ 1.3) E-4

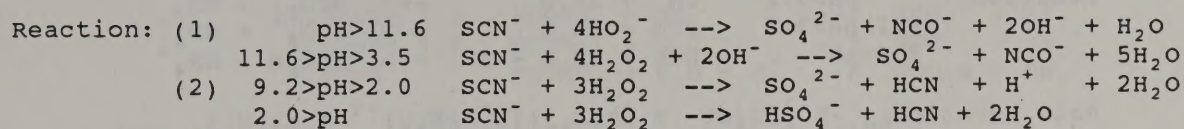
N No data.

<sup>1</sup>Estimated: not stated.

Note.—Cited references are listed at end of Chapter 7.



Table F-2.-Kinetic data for oxidation of  
thiocyanate ion by hydrogen peroxide



Rate equation: (1)  $-\text{R}^{-1}\text{Z}^{-1}\text{dZ}/\text{dt} = k_1[\text{H}^+](\text{K}_{\text{ar}} + [\text{H}^+])^{-1}$   
                  (2)  $-\text{R}^{-1}\text{Z}^{-1}\text{dZ}/\text{dt} = k_2[\text{H}^+][\text{H}_2\text{O}_2]([\text{H}_2\text{O}_2] + k_3[\text{HCN}])^{-1}$

Reported rate constants	$k_1$ 29	$k_2$ 30	$k_3$ 30
Reference			
pH range	4-13	1	1
Ionic strength., $\text{M}$	0.27	0.1	0.1
Temperature $^{\circ}\text{C}$	20-50	20, 30	20, 30
Statistical processing			
Number of points	3	2	2
Correlation coefficient	0.9998	$^1\text{N}$	$^1\text{N}$
$\Delta\text{H}^*$ , kJ	62.1 $\pm 1.2$	36.7	N
$\Delta\text{S}^*$ , J·K	-103.6 $\pm 3.8$	-151.4	N
Authors' data			
$\Delta\text{H}^*$ or $\Delta\text{E}^*$ , kJ	64.9	46.0	N
$\Delta\text{S}^*$ , J·K	E	E	N
Calculated rate constants			
0 $^{\circ}$ C	(3.0 $\pm$ .2) E-5	(6.8) E-3	N
10	(8.1 $\pm$ .4) E-5	(1.24) E-2	N
25	(3.23 $\pm$ .07) E-4	(2.9) E-2	$^2\text{2}$
40	(1.12 $\pm$ .03) E-3	(6.1) E-2	N
60	(5.0 $\pm$ .2) E-3	(1.51) E-1	N
90	(3.5 $\pm$ .3) E-2	(4.9) E-1	N

N No data.

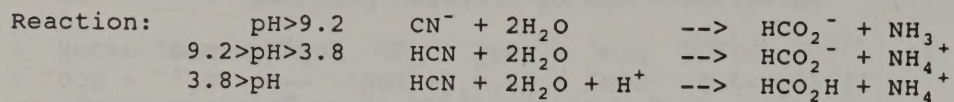
$^1$ Correlation coefficient and errors not determinable.

$^2$ Approximately constant at 20 $^{\circ}$  and 30 $^{\circ}$  C.

Note.—Cited references are listed at end of Chapter 7.



Table F-3.-Kinetic data for addition of water to cyanide



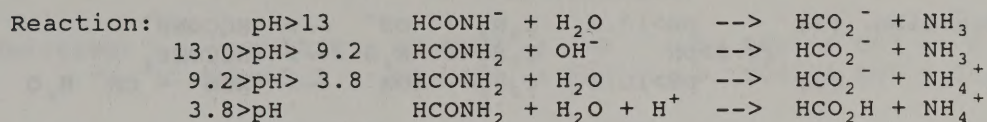
Rate equation:  $-Z^{-1}dZ/dt = k_1 K_{az} ([\text{H}^+] + K_{az})^{-1} + k_2 [\text{H}^+]$

Reported rate constants	$k_1$	$k_2$
Reference	44	47
pH range	7-10	<0
Ionic strength, $M$	0.2	6.
Temperature, $^{\circ}\text{C}$	30-100	70-85
Statistical processing		
Number of points	3	3
Correlation coefficient	1.0000	0.9999
$\Delta H^*$ , kJ	95.1	74.9
	$\pm 8$	$\pm 9$
$\Delta S^*$ , J·K	-79.2	-116.4
	$\pm 2.4$	$\pm 2.7$
Authors' data		
$\Delta H^*$ or $\Delta E^*$ , kJ	N	77.8
$\Delta S^*$ , J·K	N	E
Calculated rate constants		
0 $^{\circ}$ C	(2.7 $\pm$ .2) E-10	(2.3 $\pm$ .2) E-8
10	(1.26 $\pm$ .07) E-9	(7.7 $\pm$ .6) E-8
25	(1.01 $\pm$ .05) E-8	(4.0 $\pm$ .2) E-7
40	(6.7 $\pm$ .2) E-8	(1.78 $\pm$ .07) E-6
60	(6.3 $\pm$ .2) E-7	(1.07 $\pm$ .02) E-5
90	(1.18 $\pm$ .04) E-5	(1.08 $\pm$ .01) E-4

N No data.

Note.—Cited references are listed at end of Chapter 7.

Table F-4.--Kinetic data for hydrolysis of formamide



Rate equation:  $-Z^{-1}dz/dt = k_1[\text{H}^+] + k_2 + k_3[\text{OH}^-]$

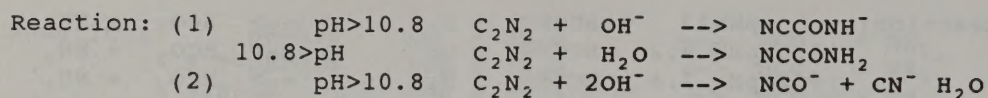
Reported rate constants	$k_1$	$k_2$
Reference	62	61
pH range	1-9	1-9
Ionic strength, M	0.1	0.1
Temp., °C	80 only	80 only
Statistical processing		
Number of points	N	N
Correlation coefficient		
$\Delta H^*$ , kJ	N	N
$\Delta S^*$ , J·K	N	N
Authors' data		
$\Delta H^*$ or $\Delta E^*$ , kJ	N	N
$\Delta S^*$ , J·K	N	N
Calculated rate constants		
0° C	(1.05±.21) E-5	(1.66±.09) E-4
10	(3.33±.47) E-4	(4.8±1.8) E-3
25	(1.63±.11) E-4	(2.10±.35) E-3
40	(6.83±0.32) E-4	(8.0±.9) E-3
60	(3.8±0.4) E-3	(3.9±1.1) E-2
90	(3.5±0.8) E-25	(3.1±1.9) E-14

N No data.

Note.—Cited references are listed at end of Chapter 7.



Table F-5.-Kinetic data for hydrolysis of cyanogen



Rate equation: (1)  $-Z^{-1}dz/dt = k_1 + k_2K_w[H^+]^{-1}$   
                  (2)  $-Z^{-1}dz/dt = k_3K_w[H^+]^{-1}$

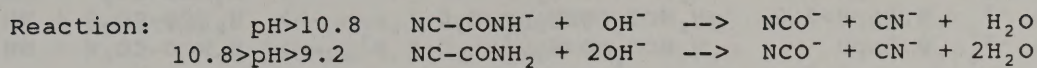
Reported rate constants	$k_1$	$k_2$	$k_3$
Reference	67	67	67
pH range	2.0	11-13	11-13
Ionic strength, M	0.01	0.01	0.01
Temperature, °C	25	5-45	5-45
Statistical processing			
Number of points	N	8	8
Correlation coefficient	N	0.9999	0.9999
$\Delta H^\ddagger$ , kJ	N	55.2	63.7
		$\pm 3$	$\pm 4$
$\Delta S^\ddagger$ , J·K	N	+4.4	+25.5
		$\pm 1$	$\pm 1.3$
Authors' data			
$\Delta H^\ddagger$ or $\Delta E^\ddagger$ , kJ	N	55.3	63.8
		$\pm 3$	$\pm 4$
$\Delta S^\ddagger$ , J·K	N	-33.8	-12.1
		$\pm 3$	$\pm 1$
Calculated rate constants			
0° C	N	(2.65 $\pm$ .08) E+2	(8.2 $\pm$ .3) E+1
10	N	(6.48 $\pm$ .12) E+2	(2.28 $\pm$ .05) E+2
25	<sup>1</sup> 5.3E-7	(2.22 $\pm$ .03) E+3	(9.35 $\pm$ .14) E+2
40	N	(6.79 $\pm$ .15) E+3	(3.38 $\pm$ .09) E+3
60	N	(2.58 $\pm$ .10) E+4	(1.55 $\pm$ .07) E+4
90	N	(1.46 $\pm$ .09) E+5	(1.13 $\pm$ .09) E+5

N No data.

<sup>1</sup>Reported.

Note.—Cited references are listed at end of Chapter 7.

Table F-6.--Kinetic data for disproportionation  
of cyanoformamide



Rate equation:  $-Z^{-1}dZ/dt = k_1 K_{az}([H^+] + K_{az})$

Reported rate constants	$k_1$
Reference	67
pH range	11-13
Ionic strength, $\underline{M}$	0.01
Temperature, °C	5-45
Statistical processing	
Number of points	5
Correlation coefficient	<sup>1</sup> N
$\Delta H^*$ , kJ	<sup>1</sup> N
$\Delta S^*$ , J·K	<sup>1</sup> N
Authors' data	
$\Delta H^*$ or $\Delta E^*$ , kJ	91.8 ±.4
$\Delta S^*$ , J·K	+57.7 ±.3
Calculated rate constants	
0° C	<sup>2</sup> (1.64) E-2
10	<sup>2</sup> (7.1) E-2
25	<sup>2</sup> (5.3) E-1
40	<sup>2</sup> (3.28)
60	<sup>2</sup> (2.90) E+1
90	<sup>2</sup> (4.9) E+2

N No data.

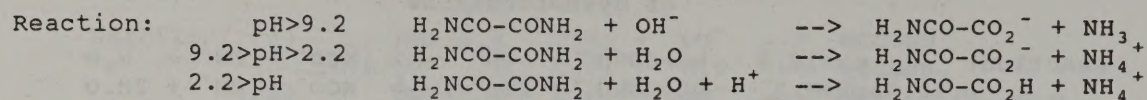
<sup>1</sup>Individual rate constants not reported.

<sup>2</sup>Calculated from authors' activation parameters.

Note.—Cited references are listed at end of Chapter 7.



Table F-7.-Kinetic data for hydrolysis of oxamide



Rate equation:  $-Z^{-1}dz/dt = k_1[\text{H}^+] + k_2[\text{OH}^-]$

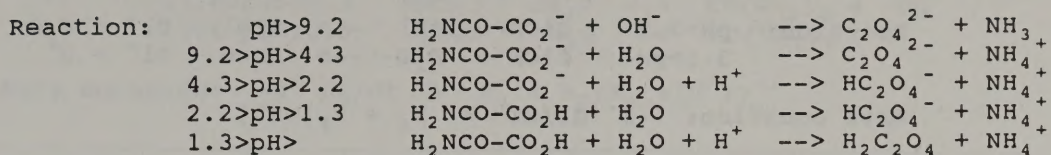
Reported rate constants	$k_1$	$k_2$
Reference	78	79, 80
pH range	0-2	12-13
Ionic strength, M	1.	1.
Temperature, °C	80, 98	0-30
Statistical processing		
Number of points	2	4
Correlation coefficient	<sup>1</sup> N	0.9994
$\Delta H^*$ , kJ	79.2	38.3
		±1.0
$\Delta S^*$ , J·K	-86.4	-149.8
		±3.3
Authors' data		
$\Delta H^*$ or $\Delta E^*$ , kJ	86	38.9
$\Delta S^*$ , J·K	E	-156.9
Calculated rate constants		
0° C	(1.2) E-7	(4.0±.2) E-3
10	(4.4) E-7	(7.6±.2) E-3
25	(2.5) E-6	(1.81±.05) E-2
40	(1.22) E-5	(4.0±.2) E-2
60	(8.1) E-5	(1.03±.08) E-1
90	(9.3) E-4	(3.5±.4) E-1

N No data.

<sup>1</sup>Correlation coefficient and errors not determinable.

Note.—Cited references are listed at end of Chapter 7.

Table F-8.-Kinetic data for hydrolysis of oxamic acid



Rate equation:  $-Z^{-1}dZ/dt = k_1[\text{H}^+] + k_2 + k_3[\text{OH}^-]$

Reported rate constants	$k_1$	$k_1$	$k_2$	$k_3$
Reference	78	79, 80	79, 80	79, 80
pH range	0-2	0-1	0-1	13-14
Ionic strength., M	1.0	1.0	1.0	1.0
Temperature, °C	80, 98	60-98	60-98	40-60
Statistical processing				
Number of points	2	4	5	3
Correlation coefficient	<sup>1</sup> N	0.9980	0.9975	0.9997
$\Delta H^\ddagger$ , kJ	78.8	71.2 ±3.2	69.6 ±2.9	44.4 ±1.0
$\Delta S^\ddagger$ , J·K	-82.3	-103.2 ±9.1	-134.9 ±8.1	-165.8 ±3.2
Authors' data				
$\Delta H^\ddagger$ or $\Delta E^\ddagger$ , kJ	86	69.5	67.8	46.0
$\Delta S^\ddagger$ , J·K	E	-60.7	-147.7	-169.9
Calculated rate constants				
0° C	(2.5) E-7	(5.6±3.1) E-7	(2.5±1.6) E-8	(4.0±.3) E-5
10	(8.7) E-7	(1.8±.8) E-6	(7.8±4.0) E-8	(8.2±.5) E-5
25	(4.9) E-6	(8.5±2.7) E-6	(3.6±1.3) E-7	(2,24±.08) E-4
40	(2.4) E-5	(3.5±.7) E-5	(1.46±.36) E-6	(5.56±.09) E-4
60	(1.55) E-4	(1.94±.20) E-4	(7.7±1.0) E-6	(1.65±.03) E-3
90	(1.77) E-3	(1.77±.16) E-3	(6.7±.6) E-5	(6.8±.3) E-3

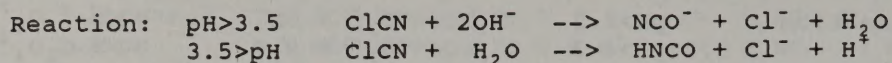
N No data.

<sup>1</sup>Correlation coefficient and errors not determinable.

Note.—Cited references are listed at end of Chapter 7.



Table F-9.-Kinetic data for hydrolysis of cyanogen chloride



Rate equation:  $-z^{-1}dz/dt = k_1 + k_2[\text{OH}^-]$

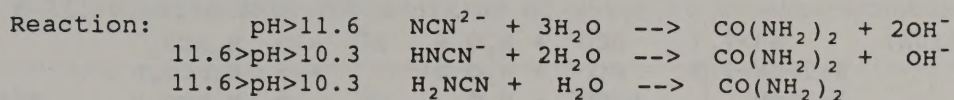
Reported rate constants	$k_1$	$k_1$	$k_2$
Reference	83	85	85
pH range	7	2-3	10
Ionic strength, $M$	0.	0.07	0.07
Temperature, $^{\circ}\text{C}$	40-60	18-41	20-40
Statistical processing			
Number of points	3	3	3
Correlation coefficient	0.9992	0.9998	0.9985
$\Delta H^{\circ}$ , kJ	80.3	84.0	85.6
	$\pm 3.2$	$\pm 1.6$	$\pm 4.6$
$\Delta S^{\circ}$ , J·K	-95.	-84.1	+63.
	$\pm 10.$	$\pm 5.2$	$\pm 15.$
Authors' data			
$\Delta H^{\circ}$ or $\Delta E^{\circ}$ , kJ	85.8	<sup>1</sup> 82, 86	<sup>1</sup> 83, 82
$\Delta S^{\circ}$ , J·K	E	<sup>1</sup> -90, -77	<sup>1</sup> 53, 52
Calculated rate constants			
0 $^{\circ}$ C	(2.9 $\pm$ 1.7) E-8	(2.0 $\pm$ 1.2) E-8	(4.7 $\pm$ 1.1) E-1
10	(1.0 $\pm$ 1.2) E-7	(7.7 $\pm$ 1.4) E-8	(1.9 $\pm$ 1.3)
25	(6.1 $\pm$ 1.6) E-7	(4.9 $\pm$ 1.1) E-7	(1.22 $\pm$ 0.07) E+1
40	(3.02 $\pm$ 1.15) E-6	(2.59 $\pm$ 1.08) E-6	(6.7 $\pm$ 1.5) E+1
60	(2.04 $\pm$ 1.10) E-5	(1.91 $\pm$ 1.12) E-5	(5.1 $\pm$ 1.0) E+2
90	(2.4 $\pm$ 1.4) E-4	(2.6 $\pm$ 1.3) E-4	(7.2 $\pm$ 2.6) E+3

N No data.

<sup>1</sup>Two determinations.

Note.—Cited references are listed at end of Chapter 7.

Table F-10.--Kinetic data for addition of water to cyanamide



Rate equation:  $-Z^{-1}dZ/dt = k_1 + k_2(K_{az} + [\text{H}^+])^{-1}$

Reported rate constants	$k_2$	$k_1$	$k_1$
Reference	87	88	89
pH range	8-12	2	0
Ionic strength, $M$	0.1	0.02	1.0
Temperature, $^{\circ}\text{C}$	60-90	60, 85	25-40
Statistical processing			
Number of points	4	2	6
Correlation coefficient	0.9995	$^1N$	0.9936
$\Delta H^*$ , kJ	89.5	115.5	71.3
	$\pm 1.9$		$\pm 4.1$
$\Delta S^*$ , J·K	-69.5	+2.8	-91.
	$\pm 5.6$		$\pm 13.$
Authors' data			
$\Delta H^*$ or $\Delta E^*$ , kJ	93.7	121.	$^2N$
$\Delta S^*$ , J·K	E	E	-90
Calculated rate constants			
0 $^{\circ}$ C	(1.0 $\pm$ 1.3) E-8	(7.) E-10	(2.3 $\pm$ 1.0) E-6
10	(4.3 $\pm$ 1.1) E-8	(4.1) E-9	(7.1 $\pm$ 2.0) E-6
25	(3.1 $\pm$ 1.5) E-7	(5.1) E-8	(3.4 $\pm$ 1.3) E-5
40	(1.82 $\pm$ 0.21) E-6	(5.0) E-7	(1.43 $\pm$ 0.15) E-4
60	(1.53 $\pm$ 0.08) E-5	(7.6) E-6	(7.9 $\pm$ 2.5) E-4
90	(2.40 $\pm$ 13) E-4	(2.59) E-4	(7.2 $\pm$ 4.9) E-3

N No data.

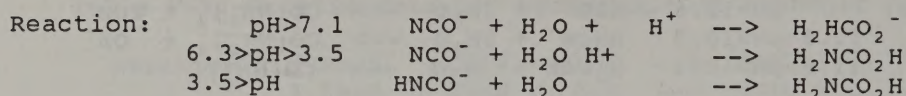
$^1$ Correlation coefficient and errors not determinable.

$^2$ Not reported.

Note.--Cited references are listed at end of Chapter 7.



Table F-11.-Kinetic data for addition of water to cyanate



Rate equation:  $-Z^{-1}dZ/dt = k_1[\text{H}^+]^2(\text{K}_{\text{az}} + [\text{H}^+])^{-1} + k_2\text{K}_{\text{az}}[\text{H}^+](\text{K}_{\text{az}} + [\text{H}^+])^{-1} + k_3$ ;  $k_2' = k_2\text{K}_{\text{az}}$

Reported rate constants	$k_1$	$k_2'$	$k_3$	$k_2$
Reference	20	20	20	97
pH range	0	2-5	12-13	8-11
Ionic strength, $\text{M}$	1.0	0.1	0.3	0.25
Temperature, $^{\circ}\text{C}$	1-26	0-12	65-100	60, 80
Statistical processing				
Number of points	3	3	3	2
Correlation coefficient	0.9997	0.9993	1.0000	$^{1}\text{N}$
$\Delta\text{H}^*$ , kJ	59.0	63.6	96.7	58.1
	$\pm 1.4$	$\pm 2.4$	$\pm 1.7$	
$\Delta\text{S}^*$ , J·K	-64.9	-83.2	+70.0	-36.4
	$\pm 4.9$	$\pm 8.6$	$\pm 1.9$	
Authors' data				
$\Delta\text{H}^*$ or $\Delta\text{E}^*$ , kJ	61.	67.	98.	61.1
$\Delta\text{S}^*$ , J·K	E	E	E	-36.9
Calculated rate constants				
0° c	(1.22 $\pm$ .04) E-2	(1.80 $\pm$ .05) E-4	(4.1 $\pm$ .3) E-10	(5.4) E-1
10	(3.16 $\pm$ .07) E-2	(5.0 $\pm$ .1) E-4	(1.9 $\pm$ .1) E-9	(1.39)
25	(1.17 $\pm$ .04) E-1	(2.1 $\pm$ .2) E-3	(1.58 $\pm$ .07) E-8	(5.1)
40	(3.9 $\pm$ .2) E-1	(7.4 $\pm$ .9) E-3	(1.08 $\pm$ .03) E-7	(1.64) E+1
60	(1.60 $\pm$ .14) E+1	(3.4 $\pm$ .6) E-2	(1.07 $\pm$ .02) E-6	(6.7) E+1
90	(1.01 $\pm$ .14) E+1	(2.5 $\pm$ .7) E-1	(2.08 $\pm$ .02) E-5	(4.1) E+2

Table F-11.--Kinetic data for addition of water to cyanate--Continued

Reported rate constants	$k_3$	$k_1$	$k_2'$	$k_3$
Reference	97	98	98	98
pH range	8-11	1	1-5	13
Ionic strength, $M$	0.25	0.2	0.2	0.2
Temperature, $^{\circ}C$	60, 80	4-18	10, 18	70-94
Statistical processing				
Number of points	2	3	2	3
Correlation coefficient	$^1N$	0.9998	N	0.9999
$\Delta H^*$ , kJ	100.0	60.0	80.6	97.6
		$\pm 1.1$		$\pm 1.2$
$\Delta S^*$ , J·K	-60.2	-62.0	-28.5	-67.9
		$\pm 3.9$		$\pm 3.3$
Authors' data				
$\Delta H^*$ or $\Delta E^*$ , kJ	102.9	63.2	83.3	100.0
$\Delta S^*$ , J·K	60.7	E	E	E
Calculated rate constants				
0 $^{\circ}$ C	(3.1) E-10	(1.10 $\pm$ .02) E-2	(7.2) E-5	(3.6 $\pm$ .5) E-10
10	(1.5) E-9	(2.89 $\pm$ .03) E-2	(2.62) E-4	(1.7 $\pm$ .2) E-9
25	(1.35) E-8	(1.10 $\pm$ .03) E-1	(1.54) E-3	(1.42 $\pm$ .11) E-8
40	(9.8) E-8	(3.7 $\pm$ .2) E-1	(7.7) E-3	(9.8 $\pm$ .6) E-8
60	(1.05) E-6	(1.56 $\pm$ .12) E-1	(5.2) E-2	(9.9 $\pm$ .3) E-7
90	(2.25) E-5	(1.02 $\pm$ .11) E+1	(6.3) E-1	(1.98 $\pm$ .03) E-5

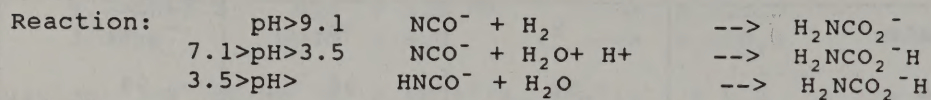
N No data.

<sup>1</sup>Correlation coefficient and errors not determinable.

Note.—Cited references are listed at end of Chapter 7.



Table F-12.--Kinetic data for bicarbonate-catalyzed addition of water to cyanate



Rate equation:  $-Z^{-1}dz/dt = k_1[\text{HCO}_3^-]$

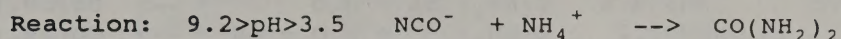
Reported rate constants	$k_1$	$k_1$
Reference	97	99
pH range	8-9	8-10
Ionic strength, $\text{M}$	0.25	0.2
Temperature, $^{\circ}\text{C}$	60, 80	18-50
Statistical processing		
Number of points	2	3
Correlation coefficient	$^1\text{N}$	1.0000
$\Delta\text{H}^*$ , kJ	65.8	65.2
		$\pm 2$
$\Delta\text{S}^*$ , J·K	-116.1	-118.4
		$\pm 6$
Authors' data		
$\Delta\text{H}^*$ or $\Delta\text{E}^*$ , kJ	67.4	67.8
$\Delta\text{S}^*$ , J·K	E	E
Calculated rate constants		
0 $^{\circ}$ C	(1.3) E-6	(1.27 $\pm$ .01) E-6
10	(3.7) E-6	(3.62 $\pm$ .02) E-6
25	(1.6) E-5	(1.53 $\pm$ .01) E-5
40	(6.0) E-5	(5.68 $\pm$ .02) E-5
60	(2.9) E-4	(2.72 $\pm$ .02) E-4
90	(2.25) E-3	(2.07 $\pm$ .02) E-3

N No data.

$^1$ Correlation coefficient and errors not determinable.

Note.—Cited references are listed at end of Chapter 7.

Table F-13.-Kinetic data for formation  
of urea from cyanate and ammonia



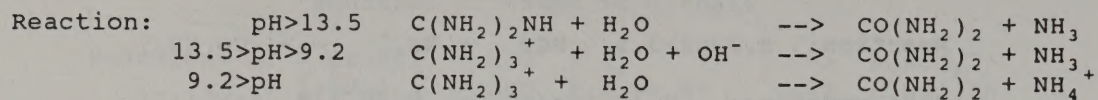
Rate equation:  $-\text{R}^{-1}\text{Z}^{-1}\text{dz}/\text{dt} = k_1[\text{H}^+](K_{a_z} + [\text{H}^+])^{-1}$

Reported rate constants	$k_1$
Reference	90
pH range	8-9
Ionic strength, $\text{M}$	0.25
Temperature, $^{\circ}\text{C}$	60, 80
Statistical processing	
Number of points	2
Correlation coefficient	$^1\text{N}$
$\Delta H^*$ , kJ	94.9
$\Delta S^*$ , J·K	-16.5
Authors' data	
$\Delta H^*$ or $\Delta E^*$ , kJ	97.5
$\Delta S^*$ , J·K	17.0
Calculated rate constants	
0° C	(4.0) E-7
10	(2.5) E-6
25	(2.0) E-5
40	(1.3) E-4
60	(1.24) E-3
90	(2.29) E-2

Note.—Cited references are listed at  
end of Chapter 7.



Table F-14.-Kinetic data for hydrolysis of guanidine ion



Rate equation:  $-Z^{-1}dz/dt = k_1 K_{az} [\text{OH}^-] (K_w + K_{az} [\text{OH}^-])^{-1}$

Reported rate constants	$k_1$	$k_1 K_{az} / K_w$
Reference	104	105
pH range	14	12
Ionic strength, $\underline{M}$	3.0	0.04
Temperature, °C	15-78	100-135
Statistical processing		
Number of points	<sup>1</sup> N	3
Correlation coefficient	<sup>1</sup> N	0.9999
$\Delta H^*$ , kJ	<sup>1</sup> N	130.4
		$\pm 1.4$
$\Delta S^*$ , J·K	<sup>1</sup> N	+33.9
		$\pm 3.5$
Authors' data		
$\Delta H^*$ or $\Delta E^*$ , kJ	85.4	133.5
$\Delta S^*$ , J·K	E	E
Calculated rate constants		
0° C	(5.2) E-8	(3.9 $\pm$ .8) E-11
10	(1.9) E-7	(3.1 $\pm$ .6) E-10
25	(1.21) E-6	(5.3 $\pm$ .8) E-9
40	(6.3) E-6	(6.9 $\pm$ .8) E-8
60	(4.5) E-5	(1.48 $\pm$ .12) E-6
90	(5.7) E-4	(7.9 $\pm$ .3) E-5

N No data.

<sup>1</sup>Rate constant reported only for 60° C.

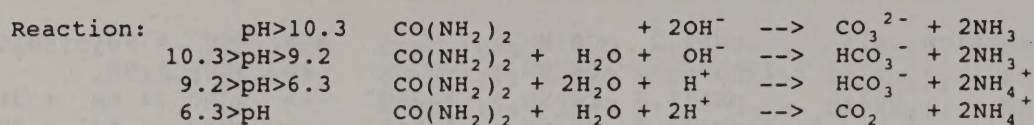
Calculated rate constants from this value and authors'  $\Delta E^*$ .

Note.—Cited references are listed at end of Chapter 7.





Table F-16.--Kinetic data for hydrolysis of urea



$$\text{Rate equation: } -Z^{-1}dz/dt = k_1 + k_2[\text{OH}^-] + k_3[\text{OH}^-]^2$$

Reported rate constants	$k_1$	$k_2$	$k_1$	$k_1$	$k_3$
Reference	88	105	109	110	110
pH range	2	12	1-7	14	14
Ionic strength, M	0.02	0.04	0.1	2.0	2.0
Temperature, °C	60, 85	90-120	60-100	33-70	
Statistical processing					
Number of points	2	3	6	4	6
Correlation coefficient	$^1\text{N}$	0.9996	0.9997	0.9905	0.9864
$\Delta\text{H}^*$ , kJ	134.3	105.8	133.5	93.5	85.7
		$\pm 2.9$	$\pm 1.6$	$\pm 7.5$	$\pm 7.1$
$\Delta\text{S}^*$ , J·K	+29.7	-53.5	+26.8	-85.	-112.
		$\pm 7.7$	$\pm 4.5$	$\pm 23.$	$\pm 22.$
Authors' data					
$\Delta\text{H}^*$ or $\Delta\text{E}^*$ , kJ	N	108.8	136.8 $\pm 9$	90.3	89.9
$\Delta\text{S}^*$ , J·K	E	E	E	-83.7	-89.5
Calculated rate constants					
0° C	(4.0) E-12	(5. $\pm$ 2.) E-11	(4.2 $\pm$ 1.6) E-12	$^3\text{N}$	$^3\text{N}$
10	(3.5) E-11	(2.9 $\pm$ 1.0) E-10	(3.4 $\pm$ 1.1) E-11	$^3\text{N}$	$^3\text{N}$
25	(6.5) E-10	(2.9 $\pm$ 1.8) E-9	(6.3 $\pm$ 1.5) E-10	(1.0 $\pm$ 1.6) E-8	(9. $\pm$ 6.) E-9
40	(9.2) E-9	(2.4 $\pm$ 1.5) E-8	(8.7 $\pm$ 1.4) E-9	(6.2 $\pm$ 1.9) E-8	(5.0 $\pm$ 1.6) E-8
60	(2.16) E-7	(2.9 $\pm$ 1.4) E-7	(2.02 $\pm$ 1.18) E-7	(5.7 $\pm$ 1.5) E-7	(3.8 $\pm$ 1.1) E-7
90	(1.29) E-5	(7.4 $\pm$ 1.4) E-6	(1.18 $\pm$ 1.06) E-5	$^1\text{N}$	$^1\text{N}$

N No data.

$^1$ Correlation coefficient and errors not determinable.

$^2$ Not reported.

$^3$ Error larger than value.

Note.—Cited references are listed at end of Chapter 7.

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